

1/2D SnO₂ nanowires on MnO₂ nanosheets hybrid architecture for reducing fire hazards of epoxy nanocomposites

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ABSTRACT

SnO₂ nanowires decorated MnO₂ nanosheets hybrids, were prepared and incorporated into epoxy resins to improve the flame retardancy and inhibit the smoke in combustion. SnO₂-MnO₂ hybrids shows significant improve in flame retardancy, fire toxicity and thermal properties of epoxy nanocomposites, compared to neat epoxy and nanocomposites with a single SnO₂ or MnO₂. The char residues and glass transition temperature of the epoxy/2 wt% SnO₂-MnO₂ nanocomposite were remarkably increased. The peak heat release rate of EP/2 wt% SnO₂-MnO₂ was significantly decreased by 62.9% than that of pure epoxy. TG-FTIR results that the concentration of organic volatiles of epoxy was significantly reduced and the toxic CO was suppressed after incorporating SnO₂-MnO₂. The physical barrier for SnO₂-MnO₂ hybrids and the synergism between the catalysis effect of SnO₂ and MnO₂ can improve the flame retardancy of epoxy resin.

1. Introduction

Epoxy (EP) as a thermoset polymer has been extensively used in many applications. They range from a coating, potting, electronic/electrical insulation, and composite applications, which are characterized by its unusual mechanical stiffness and toughness, good solvent and chemical resistance, excellent thermal and mechanical stabilities, and superior adhesion [1–4]. However, its intrinsic flammability and large amount of toxic smoke reduces its practical application. In this context, it is of great significance to reduce the overall fire hazards of EP. Various approaches have been developed to improve the fire resistance of EP. In the existing research, halogen-containing flame retardants are economic and effective flame retardants for EP. However, a considerable problem for halogen-containing flame retardants is their produced black smoke and corrosive gases during burning [5,6]. Accordingly, the development of halogen-free flame retardant EP resin has a great advantage and development potential.

In last few decades, nanocomposite technology has proven particularly useful in the flame retardant research [7]. The use of nanofillers, such as layered silicates, layered double hydroxides, carbon based-materials (expanded graphite, fullerene, and carbon nanotubes), silica and polyhedral oligomeric silsesquioxanes nanoparticles can efficiently improve the gas permeability, flame retardancy, and thermal stability

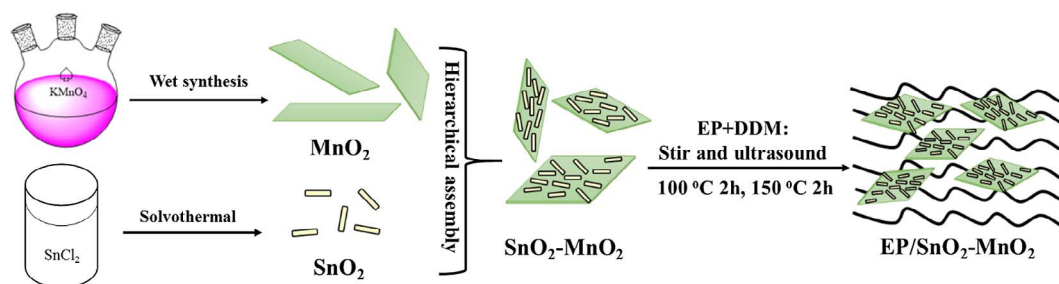
of polymer nanocomposites [8–10].

Among all the nanoadditives, metal compounds, especially transition metal elements such as nickel [11], cobalt [12], and titanium [13] exhibit good efficiency in improving fire retardancy of polymers by catalyzing the formation of graphitized char during combustion. Our previous studies have indicated that metal oxides have a major impact on thermal stability, flame retardancy and the smoke suppression of polymer [13]. Wu et al. fabricated TiO₂ nanotube has high efficiency to improve the thermal stability of EP, and Hong et al. highlighted the addition of Co₃O₄ and NiO for smoke suppression in polyamide 6 [14,15].

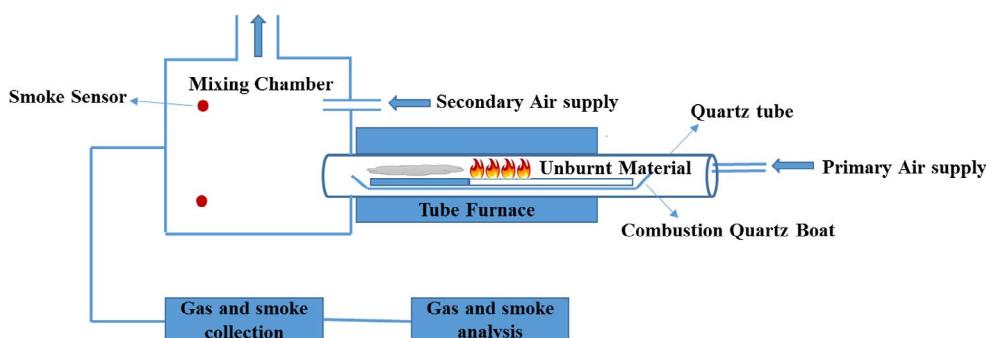
It has long been known that hybrid nanofillers made by combining two or more kinds of unit or two different filler geometries of different length scales can sometimes achieve a synergistic effect and a superior mechanical, electrical, and thermal conductivity properties of the polymer nanocomposites [11,15–18]. Besides the combination of their individual properties, the hybrid nanofillers obtain especial joint catalytic properties compared with single-component materials [19]. Feng's research work suggested the combining of MoS₂ with CoOOH not only catalyzed carbonization of the degradation products, but also reduce the hazards of toxic products and obvious smoke suppression of EP [12].

As a result, the metal compounds containing two types of transition

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Scheme 1. Illustration for the formation mechanism of $\text{SnO}_2\text{-MnO}_2$ hybrids and preparation of EP/ $\text{SnO}_2\text{-MnO}_2$ nanocomposites. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Scheme 2. The diagrammatic illustration of the steady state tube furnace. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

metal elements is an effective strategy for enhancing the flame retardant and inhibiting smoke release of polymer during combustion. Accordingly, the joint of nanocomposite technique and metal compounds provides a new way to obtain reliable fire safety performance of polymers. The popularity of MnO_2 as a functional metal oxide is due to its distinctive physical and chemical properties and extensively used in adsorption [20], catalysis [21], and flame retardation [22]. Manganese oxide (MnO_2) nanosheets, with a specific surface area, can be used as a supporter for nanofillers to ensure good dispersion, that resemble to MnOOH nanorods/graphene [23], V_2O_5 nanowire/graphene [24], and TiO_2 nanowire/graphene [25]. Stannic oxide (SnO_2) or other stannum compounds have been used in many polymers, such as EP [26], polyester [27], ABS [28], PVC [29], and the flame retardant property is often adequate. It was anticipated that SnO_2 /graphene hybrids could reduce the organic volatiles of EP and suppress the toxic CO [26]. Cusack et al. [30,31] confirmed that the flame-retardant and smoke-suppressant effects of zinc hydroxystannate and zinc stannate in polymer resin. Furthermore, Qu et al. [32] reported that tin dioxide, and tin monoxide acted as flame retardant and smoke retardant for poly-vinyl chloride. Overall, combined with MnO_2 and SnO_2 , can significantly enhance the fire safety of EP, which has seldom been studied.

In this work, SnO_2 nanowires decorated MnO_2 nanosheets hybrids have been prepared and added into EP matrix. The dispersion state of the hybrids, thermal behavior and fire hazards of the EP nanocomposites were investigated. The mechanism for the reduced fire hazards of EP was proposed. It is expected that SnO_2 nanowires decorated MnO_2 nanosheets hybrids materials will provide a promising strategy to reduce the fire hazards of polymers.

2. Experimental

2.1. Materials

Oleylamine (80–90% C18 contents) was supplied by Shanghai Aladdin Bio-Chem Technology Co., Ltd. (China) Potassium permanganate (KMnO_4), ethyl acetate, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, oleic acid, tetrahydrofuran (THF), 4,4'-diaminodiphenylmethane (DDM), acetone and anhydrous ethanol were from Sinopharm Chemical Reagent Co., Ltd. Bisphenol-A type EP resin was received from Nantong Xingchen Synthetic Material

Co., Ltd. (Jiang Su, China). The deionized water was used throughout the experiment.

2.2. Synthesis of MnO_2 nanosheets

KMnO_4 (2.37 g) was dissolved in 750 mL deionized water and then 200 mL of ethyl acetate was added into the solution. The resulted solution was heated to 85 °C and refluxed for an adequate time. The purple color of KMnO_4 faded and the brown MnO_2 precipitate was produced. The brown product was filtrated and washed with deionized water and absolute ethanol consecutively and dried at 60 °C under vacuum overnight. Then, the MnO_2 nanosheets could be obtained [33].

2.3. Synthesis of SnO_2 nanowires

In a typical procedure, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (1.75 g), oleylamine (2.68 g), oleic acid (11.30 g) and absolute ethanol (4.61 g) were taken together in a 35 mL glass cup and stirred for 10 min. Then the glass cup was transferred to a 100 mL Teflon-lined stainless steel autoclave containing 19.2 mL ethanol solution and 0.8 mL water and maintained at 180 °C for 18 h. The resulting SnO_2 nanowires were centrifuged, washed with absolute ethanol and finally dried at 60 °C [34].

2.4. SnO_2 nanowires loaded on MnO_2 nanosheets- $\text{SnO}_2\text{-MnO}_2$ nanohybrid

The SnO_2 nanowires loaded on the MnO_2 nanosheets was prepared using a van der Waals interactions methodology [35]. Briefly, 0.2 g SnO_2 nanowires and 0.3 g MnO_2 were dispersed in THF and sonicated for 12 h. The resulting $\text{SnO}_2\text{-MnO}_2$ hybrids were filtrated using a 0.22 μm PTFE membrane, followed by vacuum-drying at 60 °C.

2.5. Preparation of EP and EP nanocomposites

The solution blending method was used to prepare the EP/2 wt% $\text{SnO}_2\text{-MnO}_2$ nanocomposite. The EP nanocomposite was prepared as follows: the $\text{SnO}_2\text{-MnO}_2$ was added to acetone and ultrasonically stirred until the $\text{SnO}_2\text{-MnO}_2$ was completely dispersed. Then, EP resin was introduced into the abovementioned suspension with stirring for 1 h. Subsequently, the acetone was removed by a vacuum oven at 80 °C.

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