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Regular Article

Ultrathin Beta-Nickel hydroxide nanosheets grown along multi-walled carbon nanotubes: A novel nanohybrid for enhancing flame retardancy and smoke toxicity suppression of unsaturated polyester resin

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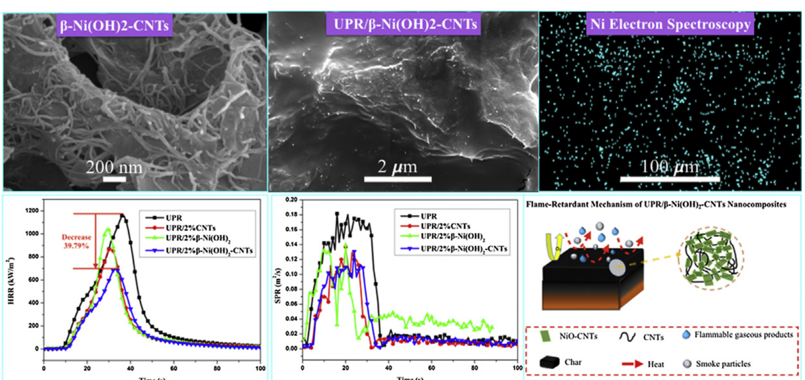
GRAPHICAL ABSTRACT



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ABSTRACT

Novel nanohybrid (β-$Ni(OH)_2$-CNTs) obtained by ultrathin Beta-Nickel hydroxide (β-$Ni(OH)_2$) nanosheets grown along multi-walled carbon nanotubes (CNTs) was successfully synthesized and then incorporated into UPR to prepare UPR/β-$Ni(OH)_2$-CNTs nanocomposites. Structure of β-$Ni(OH)_2$-CNTs nanohybrid was confirmed by X-ray diffraction, scanning electron microscopy measurements. Compared with single CNTs or β-$Ni(OH)_2$, the dispersion of β-$Ni(OH)_2$-CNTs in UPR was improved greatly. And the UPR/β-$Ni(OH)_2$-CNTs nanocomposites exhibited significant improvements in flame retardancy, smoke suppression, and mechanical properties, including decreased peak heat release rate by 39.79%, decreased total heat release by 44.87%, decreased smoke release rate by 29.86%, and increased tensile strength by 12.1%. Moreover, the amount of toxic volatile from UPR nanocomposites decomposition was dramatically reduced, and smoke generation was effectively inhibited during combustion. The dramatical reduction of fire hazards can be ascribed to the good dispersion, the catalytic charring effect of β-$Ni(OH)_2$ nanosheets and physical barrier effect of stable network structure consisted of β-$Ni(OH)_2$ and CNTs.

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1. Introduction

Unsaturated Polyester Resin (UPR) is one of the most important polyester, which are widely used in fields such as ships, building materials owing to its excellent mechanical properties, electrical properties, and chemical resistance [1–3]. However, UPR is highly flammable and always releases toxic smoke during combustion, which greatly restricts its application [4]. In previous work, the flame retardancy of UPR can be promoted by adding halogen-containing flame retardants. However, it will cause toxic and corrosive gases during combustion, which brings secondary damage to the environment and human beings [5,6]. Hence, it is of far-reaching significance for the development of new environment-friendly flame retardants.

Polymer/inorganic nanocomposites technology are an effective and green method to reduce fire hazards of polymers. With the addition of only small amounts of nanoparticles, the mechanical properties, thermal stability, flame retardant properties are dramatically enhanced [7]. Recently, nanoparticles such as nanoclays, carbon nanotubes, molybdenum disulphide, and graphene have attracted great attentions due to their superior structure, mechanical, and thermal properties [8–10]. Among those nanoparticles, carbon nanotubes (CNTs) are ideal 1-D reinforcing nanofiller for functional polymer nanocomposites. According to the available literature, the unique network structure of carbon nanotubes could form a compact carbon layer during polymer combustion, which could act an outstanding barrier to hinder the transmission of energy and inhibit the release of combustible volatiles [11,12]. Thus, carbon nanotubes have become a popular candidate on improving the flame retardancy of polymers.

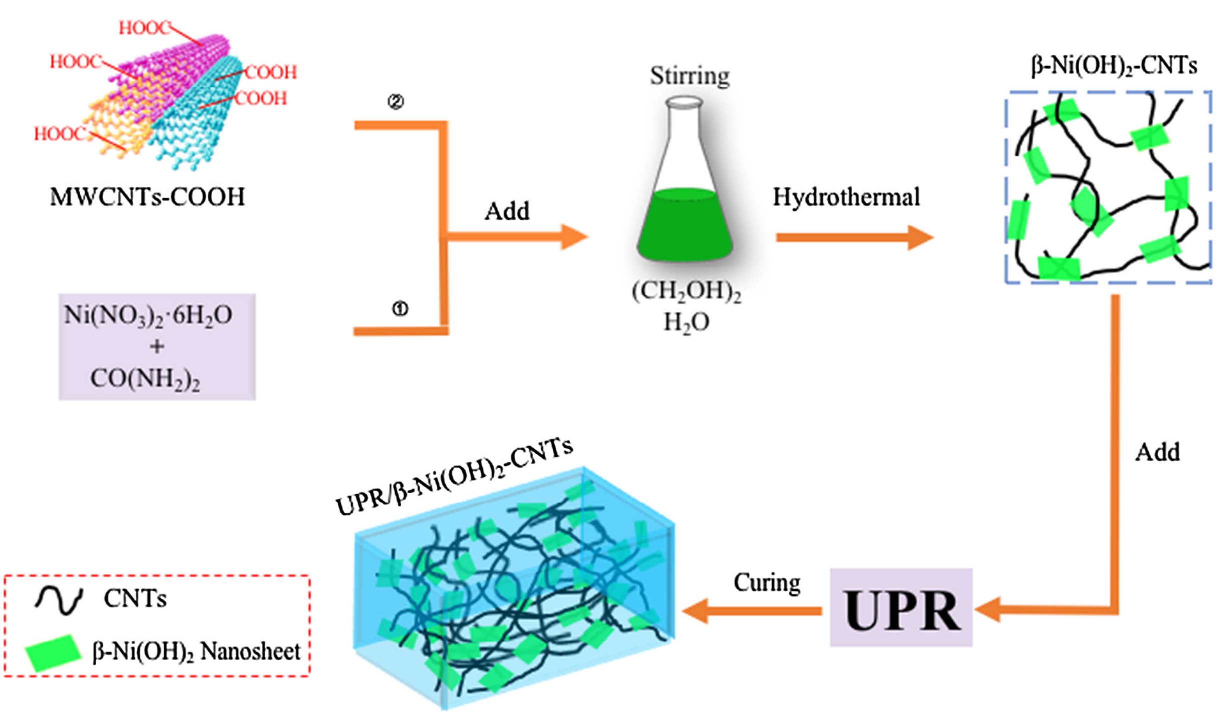
Additionally, 2-D nanoadditives, such as graphene, molybdenum sulphide, and montmorillonite, are another class of remarkable flame-retardant nanofillers [8–10,13]. Among these 2-D nanomaterials, β-Ni$(OH)_2$ nanosheets have relatively high specific areas and ultrathin thickness, tensile strength, and resilience [14]. Furthermore, most nickeliferous compounds are good catalysts for the char formation of polymers [15–18]. As described in our previous studies, β-Ni$(OH)_2$ nanosheets could catalyze the formation of graphite carbon during the thermal degradation of polymers [14,19], which have outstanding thermal stability and strength. The compact network structure of graphite carbon can obviously restrain heat transfer and the release of combustible volatiles [20–22]. Besides, the β-Ni$(OH)_2$ nanosheets have also been exhibited as a good smoke suppression agent, which is conducive to reducing the fire hazards of polymers [20–25]. However, the strong van der Waals force among nanofillers, such as CNTs and β-Ni$(OH)_2$ nanosheets, make them easy to agglomerate in the polymer matrices, which would greatly limit the final properties of polymer nanocomposites. To optimize the performances of nanofillers in the nanocomposites, it is very significant to promote their dispersion in the polymer matrix [26–29]. According to previous works, the formation of nanohybrids by combining different nanoparticles may bring better dispersion for the nanoparticles in polymers [27–29].

Herein, a novel hybrid fabricated by 2-D β-Ni$(OH)_2$ nanosheets grown along 1-D CNTs has been successfully synthesized and then introduced into UPR matrix to form new UPR/β-Ni$(OH)_2$-CNTs nanocomposites (Scheme 1). β-Ni$(OH)_2$-CNTs hybrid exhibit better dispersity in the UPR matrix. Compared with pure UPR, the UPR/β-Ni$(OH)_2$-CNTs nanocomposites was enhanced obviously in thermal property, flame retardancy, smoke suppression, and mechanical properties. Through adding 2.0 wt% β-Ni$(OH)_2$-CNTs hybrid, the peak heat release rate (PHRR), total heat release (THR), and smoke release rate (SPR) were decreased dramatically. In addition, the total volatile organic compound from thermal decomposition of the nanocomposites was reduced evidently, and quantity of aromatic compounds and hydrocarbon also were declined obviously. Thus the fire risk was reduced immensely. Also, the better tensile strength of the nanocomposites was endowed by β-Ni$(OH)_2$-CNTs hybrid. The detailed performance improvement mechanisms were proposed.

2. Experimental section

2.1. Raw material

Carboxylated multi-walled carbon nanotubes (CNTs, the degree of purity >95.0%) was obtained from the Chinese Academy of



Scheme 1. Schematic illustration for preparation of UPR/β-Ni$(OH)_2$-CNTs nanocomposites.