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The flame retardancy of blob-like multi-walled carbon nanotubes/silica nanospheres hybrids in poly (methyl methacrylate)

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ABSTRACT

Multi-walled carbon nanotubes (MWNTs) were grafted with poly (acrylic acid), and subsequently coated with a close-packed layer of silica nanospheres, namely SiO_2-g-MWNTs. Such blob-like MWNTs/silica nanospheres hybrids were introduced into poly (methyl methacrylate) (PMMA) as a kind of flame retardant. From determinations of thermogravimetric analysis and cone calorimeter tests, it was indicated that the SiO_2-g-MWNTs not only increased the initial degradation temperature and the maximum weight loss rate temperature of PMMA, but also decreased the peak of heat release rate. Observation using scanning electron microscopy revealed that the silica nanospheres on the surface of MWNTs strengthened the protective network layer during combustion.

1. Introduction

With the development of the nanotechnology, more and more researches demonstrated that the nanoparticles played an important role on the improvement of the thermal stability and flame retardancy of polymers [1]. Clay, layered double hydroxides (LDH), carbon nanotubes (CNTs), and some metal oxides were considered as effective modifiers by many researchers [2–9]. Kim et al. [10] found that the combination of nanoclay and triphenyl phosphate (TPP) brought a decrease in the peak of heat release rate (PHRR) and an increase in the average specific extinction area (ASEA, related to smoke production). Calistor et al. [11] found that MgAl-LDH enhanced the thermal stability of poly (methyl methacrylate) (PMMA) and reduced the PHRR significantly. Both Kashiwagi and Schartel teams [12–14] did a large quantity of research on the flammability of polymer/CNTs composites. Kashiwagi discussed the flame retardancy mechanisms of polymer/CNTs, and studied the effect of concentration, dispersion [15], and aspect ratio of CNTs [16] on the flammability of polymer composites. A good dispersion and certain concentration of CNTs could effectively reduce the PHRR and form a continuous layer. Schartel [17,18] studied the relationship between viscoelastic and flammability. With the introduction of CNTs, the increased melt viscosity could influence the fire behavior of the polymer composites. They also assessed the fire performance of composites under different fire scenarios. In addition, Beyer [19,20] researched the synergy effects between CNTs and organoclay on flame retardancy of polymer composites. It was believed that a continuous and network structure protective layer was essential for the significant reduction in the heat release rate.

In recent works, it was exhibited that CNTs improved the thermal stability and flame retardancy of polymers more effectively [21–24]. Moreover, the dispersion of CNTs in polymer matrix constituted a key point in the flame retardancy performance was indicated [12]. Song et al. [25] and Ma et al. [26] compared the dispersion of pristine CNTs with CNTs wrapped with an intumescent flame retardant (IFR) in polypropylene, and showed that the IFR wrapping resulted in better flame retardancy and mechanical properties. Wang et al. [27] grafted multi-walled carbon nanotubes (MWNTs) with 9,10-dihydro-9-oxa-10-phosphaphanthrene-10-oxide/vinyl methyl dimethoxysilane and introduced the modified MWNTs in EVA. The better dispersion of MWNTs in the matrix, the better flame retardancy properties were obtained. Therefore, the modification of CNTs was necessary to effectively improve the thermal stability and flame retardancy of polymers.

PMMA, a commodity thermoplastic, has been used in a wide range of fields and applications. Its flammability (LOI = 18), however, became a drawback for some special applications [28].

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Consequently, improving the thermal stability and flame retardancy of PMMA constituted one of major interests in researches.

In this work, the blob-like MWNTs/silica nanospheres hybrids were designed and prepared. Firstly, MWNTs were grafted with poly (acrylic acid) (PAA), which provided numerous reactive sites and improved the dispersion of MWNTs in the polymer matrix simultaneously. A close-packed layer of silica nanospheres was subsequently coated on MWNTs via the reaction between PAA and silane coupling agent. Finally, such blob-like MWNTs/silica nanospheres hybrids were introduced into poly (methyl methacrylate) (PMMA) as a kind of flame retardant. During combustion process, a close-packed inorganic network structure formed, which was co-constructed by carbon nanotubes and silica nanoshperes. Such denser protective layer further improved the thermal stability and flame retardancy of PMMA.

2. Experimental

2.1. Materials

PMMA (Altuglas V40) was used as the matrix material. MWNTs (purity ≥ 95%, outer diameter 10–20 nm, length 5–15 μm) were provided by Shenzhen Nanotech Port, China. Acrylic acid (AA, 99%), azobisisobutyronitrile (AIBN, 99%), 3-aminopropyltriethoxysilane (APTES, 98%), tetrahydrofuran (THF, 99%), anhydrous ethanol, and acetone were supplied by Vas Chemical of China. *N*,*N*′-dicyclohexyl carbodiimide (DCC, 99%) was purchased from Tokyo Chemical Industry Co. Ltd. 4-Dimethylaminopyridine (DMAP, 99%) was purchased from Shanghai Prolong Biochemical Co. Ltd. Colloidal silica nanospheres suspension (LUDOX AS-40) was supplied by Sigma–Aldrich Co. Ltd. THF was distilled for purification before use.

2.2. Preparation of poly (acrylic acid) grafted MWNTs

A total of 2.00-g MWNTs was dispersed into 150 mL acetone in a dry 250 mL three neck flask under N_2, and then 10.0 mL acrylic acid was added into [29,30]. After sonication for 1 h, 0.30 g AIBN was added into the flask, and the polymerization was kept at 60 °C for 6 h. Finally, the product (denoted as PAA-g-MWNTs) was filtered, washed with deionized water for 5 times and dried under vacuum until constant weight. About 2.36 g PAA-g-MWNTs in the form of black powder, which contained about 1.99 g MWNTs and 0.37 g PAA, was obtained. The mass ratio of MWNTs/PAA was about 85/15, which was according to the results of TGA test (Fig 3).

2.3. Preparation of blob-like MWNTs/silica nanospheres hybrids

A total of 2.36 g PAA-g-MWNTs, 1.00 g DCC, 0.100 g DMAP, and 10.0 mL APTES were mixed in 150 mL anhydrous THF with sonication for 1 h in a round bottomed flask [31,32]. Then, the suspension was stirred at 60 °C for 24 h under N_2. The intermediate product (denoted as APTES-g-MWNTs) was filtered and washed with anhydrous THF for 5 times and dried under vacuum until constant weight.

APTES-g-MWNTs were hydrolyzed in 150 mL deionized water at 25 °C for 24 h. Subsequently 5.00 g colloidal silica suspension was introduced into the flask. The system was kept at room temperature for 24 h. Finally, the product (denoted as SiO_2-g-MWNTs) was filtered, washed with deionized water for 5 times and dried under vacuum until constant weight. About 3.91 g SiO_2-g-MWNTs which contained about 1.83 g MWNTs and 1.56 g SiO_2, in the form of black powder was obtained. The mass ratio of MWNTs/ SiO_2/PAA-APTES was about 47/39/14, which was according to the results of TGA test (Fig. 4). The whole preparation was schemed in Fig. 1.

2.4. Preparation of PMMA nanocomposites

SiO_2 nanospheres, pristine MWNTs, PAA-g-MWNTs, and SiO_2-g-MWNTs were blended with PMMA in a Haake PolyLab shear mixer, respectively. In order to keep the net MWNTs content at 2 wt%, the additive mounts of different modified MWNTs were 2 wt% pristine MWNTs, 2.37 wt% PAA-g-MWNTs, and 4.28 wt% SiO_2-g-MWNTs. The blending was carried out at 210 °C for 8 min with a rotating speed of 50 rpm. The nanocomposites were transferred to a mold

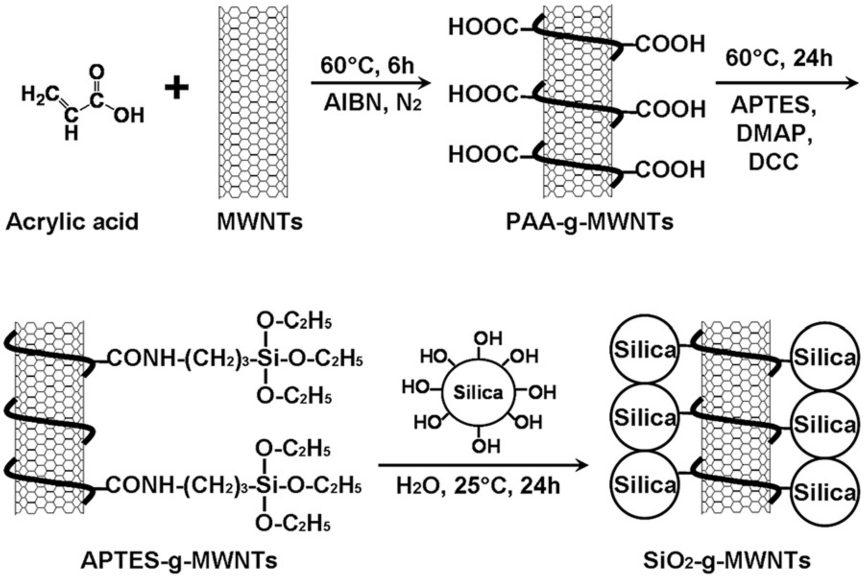

Fig. 1. Schematic illustration of the synthesis procedure of SiO_2-g-MWNTs.