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Nano-architectured mesoporous silica decorated with ultrafine Co_3O_4 toward an efficient way to delaying ignition and improving fire retardancy of polystyrene

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ABSTRACT

Aiming to impart polystyrene (PS) with delayed ignition and improved fire retardancy, mesoporous silica SBA-15 decorated with Co_3O_4 ultrafine nanoparticles (SBA-15@Co_3O_4) was nano-architectured successfully via multi-step microwave radiation approach. The design principles included: 1) SBA-15 offered the absorbing and labyrinth effect of volatiles 2) the homogeneous and ultrafine dispersion of Co_3O_4 on SBA-15 interior walls endowed more interacting sites to volatiles. In detail, the obtained SBA-15@Co_3O_4 was firstly verified using FTIR, Raman, XRD, SEM, TEM and N_2 sorption measurement. Compared with neat PS and PS/SBA-15 composites, PS composites with SBA-15@Co_3O_4 demonstrated significantly enhanced thermal and thermo-oxidation stability. Meanwhile, PS composite with 2 wt% SBA-15@Co_3O_4 (PS/2SBA-15@Co_3O_4) had a notably better fire retardancy with time to ignition (TTI) value of 116 ± 2 s, which was obviously higher than those of PS (98 ± 1 s) and PS/2SBA-15 (106 ± 1 s). Thermogravimetric analysis coupled with FTIR (TG-FTIR) and mass spectrometry (TG-MS) measurement revealed the probable mechanism of reduced heat release and delayed TTI, which was involved in the adsorption-desorption-combustion mode. Moreover, tensile test illustrated that SBA-15@Co_3O_4 notably improved the mechanical property of PS. Through this study, nano-architecture of functionalized hybrid offered a novel idea to delay ignition, decrease flammability while improve the mechanical properties for polymeric materials.

1. Introduction

Polymeric materials have enjoyed tremendous utilizations in industry community owing to their outstanding physicochemical property and ease of processing [1,2]. Among them, polystyrene (PS), as one of the five general plastics, serves a crucial role in our daily life, such as automotive and thermal-insulation panels etc. However, a serious threat is its extreme ease of flammability in the application of PS. Once PS undergoes combustion, large amounts of heat, enormous toxic and combustible gases (certain hydrocarbons etc.) and dense smoke are generated, which are vitally harmful to human health and environment. Faced with the situation, the generalized solution to alleviate the fire hazard is to incorporate proper fire retardants (nano-fillers [3–5], intrinsic [6–8] and traditional fire retardants [9–12]). Although enormous works are performed to decrease heat release and the evolution of harmful stuffs, the as-obtained fire retardant PS composites usually become easier to be ignited compared to neat PS. The reported approaches to delaying ignition behavior and improving fire retardancy predominantly concentrated on the deposition of protective coatings on polymer matrix surface [13]. Understandably, the coating method was restricted attributed to the damage to the surface physicochemical property. Accordingly, it is very necessary and urgent to intentionally delay ignition behavior and simultaneously improve fire retardancy, thermal and thermo-oxidation stability of PS composites.

Porous materials, especially mesoporous materials, showed an excellent application perspective in fire retardancy of polymer composites [14–16]. As a typical mesoporous silica material, SBA-15 possesses regularly ordered hexagonal pore structure, which was regarded to be beneficial in catalysis carbonization during combustion. Wei et al. discovered that SBA-15 provided excellent synergistic effects in intumescent flame retardant PP composites [17] and organophosphorus flame retardant PC/ABS composites [18]. It was also reported that modified SBA-15 imparted PLA with UL-94 V-0 rating even at a low loading of 0.5 wt% [14]. Based on the previous studies, it showed that SBA-15 exhibited an excellent performance in promoting fire retardancy of polymeric materials owing to the intensive catalyzing effect and adsorption-desorption effect. In addition to SBA-15, inorganic cobalt oxide (Co_3O_4) and its derivations have also been used in

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improving fire retardancy of polymeric materials. Xin et al. [19] reported that graphene doped with Co_3O_4 nanoparticles contributed to the fire safety of aliphatic polyester (PLA and PBS), decreasing the volatile evolution and CO release. Gong et al. [20] demonstrated the high-conversion preparation of mesoporous hollow carbon nanospheres with montmorillonite (MMT) and Co_3O_4 as combined catalysts.

Concerning the major objectives that are intentionally to delay TTI and improve fire retardancy of PS, SBA-15 interior walls homogeneously decorated with ultrafine Co_3O_4 nanoparticles (SBA-15@Co_3O_4) was fabricated through multi-step microwave-assisted method in order to combine the favourable functions from Co_3O_4 and SBA-15. Thermal and thermal-oxidation degradation behavior and fire behavior of as-obtained PS composites were investigated by cone calorimeter test (CCT) and TG analysis respectively. Besides, the volatile evolutions and condensed phase behavior were analyzed via thermogravimetric analysis coupled with Fourier transformation infrared spectra (TG-FTIR) and variable temperature FTIR (vt-FTIR) separately. Thermogravimetric analysis coupled with mass spectra (TG-MS) was employed to investigation mechanism for delayed TTI and improved fire retardancy. Finally, the tensile behavior of PS composites was studied.

2. Experimental

2.1. Materials

PEO_{20}-PPO_{70}-PEO_{20} (P123, M_w = 5800 g/mol), ammonium fluoride (NH_4F), hydrochloric acid (HCl, 37 wt%), heptane, traethyl orthosilicate (TEOS), urea, cobalt(II) chloride hexahydrate ($CoCl_2{\cdot}6H_2O$), polystyrene (M_w = 192,000 g/mol) was purchased from Sigma-Adrich. 1.8 M HCl aqueous solution was prepared through diluting dense HCl solution with deionized water. Deionized water was produced in our institute. All chemical agents were utilized without further purification.

2.2. Preparation of SBA-15 mesoporous silica

SBA-15 was prepared according to the reference [21]. 9.6 g of triblock copolymer Poly[(ethylene oxide)$_{20}$-b-(propylene oxide)$_{70}$-b-(ethylene oxide)$_{20}$] (P123), 0.112 g of NH_4F and 160 mL of 1.8 M HCl were charged to a single-necked flask with magnetic stirring. The temperature was kept at 17 °C stably. The vigorous stirring was maintained until P123 was fully dissolved. Subsequently, 34 mL of heptane and 11 mL of TEOS were added simultaneously and kept for 4 min. After additional 3 h static treatment, the mixture was transferred to 200 mL autoclaves and kept at 100 °C for 24 h. The resulting product was filtered and washed repeatedly for 6 times with deionized water and then dried overnight in vacuum oven. Subsequently, the product was calcined in the muffle at 550 °C for 4 h to remove the structure directing agent P123. Schematic illustration was shown in Scheme. 1.

2.3. Preparation of SBA-15@Co_3O_4 nano-architecture

10.56 g of urea and 10.24 g of $CoCl_2{\cdot}6H_2O$ were dissolved in 800 mL deionized water in a beaker with properly magnetic stirring. After clear solution was formed, 4 g of the resultant SBA-15 was added. In order to guarantee the adequate contact between the cobalt ions and interior pore walls of SBA-15, this procedure was maintained for 24 h. Then the mixture was treated in a household microwave oven with power 700 W and frequency 2450 MHz for 10 min. After that, the mixture was taken out and cooled down naturally. This procedure would be repeated additional twice in order to ensure effective reaction. Eventually, the resultant product was filtered and washed with deionized water, followed by washing with 1 M HCl solution for 3 times quickly to remove $Co(OH)_2$ on the exterior surface of SBA-15. The product was dried overnight in the vacuum oven and calcined in muffle at 320 °C for 3 h at air atmosphere. Finally, dark brown powder was obtained as the Co_3O_4 nanoparticles doped SBA-15. The specific schematic illustration was shown in Scheme. 2.

2.4. Preparation of PS composites

PS with SBA-15 and SBA-15@Co_3O_4 were prepared via melt blending at 220 °C for 3 min using micro-compounder (MC 15, Xplore). Based on this condition, series of PS composites were prepared, including neat PS, PS composites with 1 wt% and 2 wt% fractions of SBA-15 and SBA-15@Co_3O_4 with the respective labels as PS, PS/1SBA-15, PS/2SBA-15, PS/1SBA-15@Co_3O_4 and PS/2SBA-15@Co_3O_4. Subsequently, these PS composites were further hot-pressed into sheets with different dimensions for the corresponding tests.

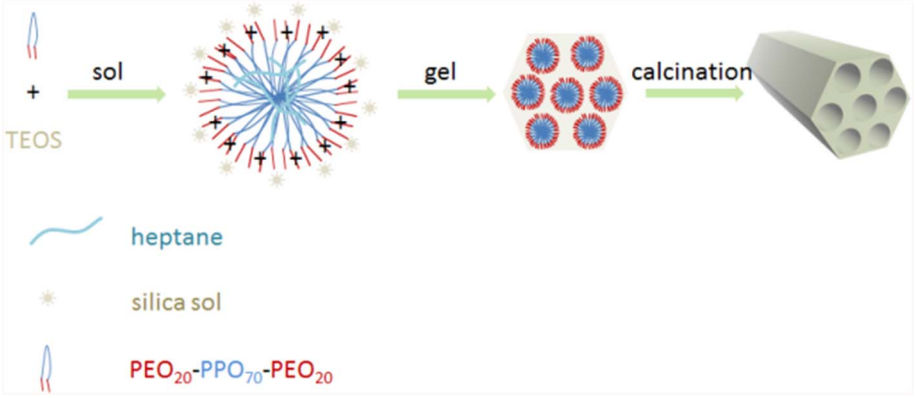
2.5. Instrumental

X-ray diffraction measurement (XRD) was performed on the XPERT-PRO diffractometer with Cu Kα radiation (λ = 0.154) and Ni filter. The secondary monochromator was used to obtain the acceptable scan.

Fourier transformed infrared spectra (FTIR) was conducted on Thermofisher Nicolet 5700 spectrometer between 400 cm^{-1} and 4000 cm^{-1}. Variable temperature FTIR (vt-FTIR) was conducted on Thermofisher Nicolet 5700 spectrometer coupled with a temperature controlling loop. PS composites thin sheet was clipped between two KBr sheets and then put in the heating supporter. The temperature was increased to 400 °C from 50 °C at 15 °C/min and then kept for another 10 min at 400 °C.

Raman spectra was recoded on RAMAN micro-spectroscopy system (Renishaw PLC) with Leica DM2700 microscope and a 532 nm Nd:YAG laser (50 mW at 532 nm) and a diffraction grating of 1800 L/mm.

N_2 sorption measurement was performed on Autosorb-1 (Quantachrome, USA). BET (Brunauer-Emmett-Teller) analysis of nitrogen isotherms at -196 °C was employed to confirm specific surface area



Scheme 1. The schematic illustration of SBA-15 preparation process.