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A novel organic-inorganic hybrid SiO_2@DPP for the fire retardance of polycarbonate

Yun-Xia Wei, Cong Deng*, Ze-Yong Zhao, Yu-Zhong Wang**

State Key Laboratory of Polymer Materials Engineering, College of Chemistry, National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), Analytical and Testing Center, Sichuan University, Chengdu 610064, China

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ABSTRACT

To enhance the fire retardance of polycarbonate (PC), a novel organic-inorganic hybrid particle containing phosphorus and silicon (SiO_2@DPP) was synthesized through a facile hydrothermal reaction. Different measurements verified that the SiO_2@DPP was prepared successfully. After incorporation of the SiO_2@DPP into PC, it was found that the flame retardancy of PC was greatly affected by only small amount of SiO_2@DPP. The PC containing only 0.8 wt% SiO_2@DPP passed the UL-94 V-0 rating in vertical combustion test and had the limiting oxygen index (LOI) of 29.3%. Moreover, the dripping behavior of PC was also restricted in this case. In cone calorimetry test, the peak heat release rate (PHRR) and the peak smoke production rate (PSPR) of PC were correspondingly remarkably reduced by 41.6% and 15.4% in the presence of only 0.8 wt% SiO_2@DPP. Moreover, the flame-retardant mechanism of the SiO_2@DPP was also investigated in detail through different measurements. The results demonstrated that the phosphorus-containing substances and SiO_2 left in the condensed phase and some structures containing phosphorus in gaseous phase had great contribution to excellent fire retardance of PC/SiO_2@DPP. All these results demonstrate that the SiO_2@DPP is an efficient organic-inorganic hybrid material for preparing fire-retardance PC.

1. Introduction

The PC, especially bisphenol A-type polycarbonate, is one of the most commonly used engineering plastics because of its excellent mechanical properties, good thermal stability, and optical transparency [1]. Although PC has the V-2 rating in the UL-94 test and the LOI of about 25% [2], showing fire retardance to a certain extent, it still cannot meet the demand on fire retardance in some application fields, particularly in electronic materials.

To meet the requirements of PC in fire safety, numerous flame-retarding techniques have been proposed, in which incorporation of additive flame retardant is an effective method [1]. Until now, numerous additive-type flame retardants have been reported, including halogen-containing compounds, phosphorus-containing compounds [3,4], sulfur-containing compounds [5], and silicon-containing compounds [2]. Halogenated flame retardants have high flame-retarding efficiency, however, they have been limited or phased out in some regions or countries because of their environmental problems and health consideration [6]. The phosphorus-containing compounds possessing good flame retardancy are one class of the most promising additive-type flame retardant for replacing the halogen-containing flame retardants in flame-retarding polymers. Triphenyl phosphate (TPP), bisphenol-A bis (diphenyl phosphate) (BDP), and resorpcinol bis (diphenylphosphate) (RDP) are three typical phosphate flame retardants for PC [7]. However, these phosphorus-containing compounds have their own disadvantages. Firstly, their additive amounts are as much as 5 ~ 15 wt% to enable PC passing the UL-94 V-0 test [7]. Secondly, these phosphorus-containing compounds, especially for phosphates, are easy to hydrolyze and have poor resistance to acid and base, which severely limit their application [8]. Finally, traditional phosphates flame retardants have relatively low initial decomposing temperature, which may deteriorate some properties of PC [9]. Flame retardants containing sulfur have also been applied in PC, such as potassium diphenylsulfone sulfonate (KSS), sodium trichlorobenzene sulfonate (STB), potassium perfluorobutane sulfonate (KPFBS) [10,11]. However, current sulfur-

* Corresponding author.
** Corresponding author.
E-mail addresses: dengcong@scu.edu.cn (C. Deng), yzwang@scu.edu.cn (Y.-Z. Wang).

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containing compounds have some drawbacks. For example, it is difficult for the PC product with thin wall to achieve good flame retardancy, and the mechanical properties of PC containing sulfur-containing compounds suffer a great loss because of the poor interfacial adhesion between flame retardants and PC matrix [12,13].

Recently, silicon-containing compounds have received more and more attention, which are regarded as "environment-friendly" flame retardants [2]. Both organic silicon and inorganic silicon as additive-type flame retardants have been reported. Oligomeric siloxane containing triphenylphosphonium phosphate (SiPP) as a type of typical organic silicon was developed in past work, showing excellent thermal stability and highly flame-retarding efficiency in PC [14]. However, the synthesis of organic silicon such as SiPP is relatively complicated, and a large number of organic solvents are necessary [2,14]. For flame retardants containing silicon (Si), the silicon dioxide (SiO_2) has been abundantly studied due to its excellent thermal stability, non-toxicity and non-generation of toxic gases during burning, and unique mechanical properties [15–17]. A novel flame retardant (ZS) containing layered a-zirconium phosphate disks (a-ZrP) and inorganic flame retardant gel-silica (GS) was prepared in the past work [18]. After incorporating the ZS into PC, it was found that the thermal stability and flame retardance of PC were improved. In a previous report [17], the synergistic catalytic effect of SiO_2@PZM@Cu was investigated in enhancing the flame retardancy of epoxy resin. Cone calorimetry result indicated that the incorporation of 2 wt% SiO_2@PZM@Cu obviously improved the flame-retardant performance of EP, such as 37.9% reduction in the peak heat release rate and 31.3% decrease in total heat release.

Although the work in blending the SiO_2 with some traditional organophosphorus flame retardants was performed in past research, but a little attention was paid to the organophosphorus modification of SiO_2, especially the modification via covalent bond. Previous researches demonstrated that the phosphorus-based compounds such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene (DOPO) and its derivatives [19], DPPA [20], ammonium polyphosphate (APP) [21,22], and so on [23], played their flame-retarding roles through different modes in polymers. In this work, we focused a novel organophosphorus silicon hybrid flame retardant SiO_2@DPP which was prepared through the chemical reaction between the SiO_2 and benzyl phosphoric acid via a sol-gel process and a following hydrothermal reaction. For the SiO_2@DPP, its structure was analyzed from different aspects. Successively, the effect of the SiO_2@DPP on the fire retardance of PC was evaluated through different combustion tests. Finally, the possible mechanism for the flame retardancy of SiO_2@DPP was proposed according to different theoretical evidences.

2. Experimental section

2.1. Materials

PC (2600) was provided from Bayer (Germany), and the used pure PC contains 0.3 wt% processing agent. TEOS (analytical grade; purity: 98%) was purchased from Chemical Technology Co., Ltd. (China); DPPA (analytical grade; purity: 98%) was purchased from Accela ChemBro Co., Ltd. (China); hydrochloric acid (analytical grade; purity: 36.0%–38.0%) was provided from Chengdu Kelong Chemical Reagent Co., Ltd. (China); acetone (analytical grade; purity: 99%) and ether (analytical grade; purity: 99%) were provided by Chengdu Changzheng Chemical Reagent Co., Ltd.(China); ethanol (EtOH; analytical grade; purity: 99%) was purchased from Chengdu Haixing Chemical Reagent Co., Ltd (China).

2.2. Synthesis of SiO_2@DPP

The SiO_2@DPP was synthesized according to Scheme 1. First, the TEOS (4.46 mL, 0.02 mol) was added in the mixture of deionied water (7.2 mL, 0.4 mol) and ethanol (23.6 mL, 0.4 mol). After 3 h, the cross-linking transparent sol-gel (SiO_2) was obtained. Then, the DPPA (4.36 g, 0.02 mol) was added in the sol-gel. Next, the solution was transferred into a 100 mL autoclave and heated to 160 °C, followed by standing for 12 h. Subsequently, the solution was cooled to room temperature (25 °C) and filtered. Next, the obtained products were washed with deionized water, ethanol, acetone, and ether several times, successively dried in a vacuum oven at 80 °C for 10 h. Finally, the SiO_2@DPP particles were obtained. According to the weighting result, the final yield was about 94%.

2.3. Preparation of PC/SiO_2@DPP composite

All raw materials were dried at 100 °C for 12 h before using. The PC/SiO_2@DPP composites were obtained by mixing the PC and different proportions of SiO_2@DPP at 255 °C under 100 rpm in a Banbury mixer (SX300, Shanghai Plastic Machinery Equipment Co. Ltd. China). The PC/SiO_2@DPP composites were used to prepare different samples through an injection machine (Mini Lab, Thermo Fisher Scientific Inc. USA) and plate vulcanizer (Qingdao Yadong Rubber Machinery Co. Ltd. China) for different tests. The ratios of PC and SiO_2@DPP are shown in Table 1.

According to Table 1, it is found that the content of SiO_2@DPP is very low. To know about its dispersion in PC matrix, the EDX test was performed. According to the structures of SiO_2@DPP and PC, it is known that the typical elemental difference between them is that only the SiO_2@DPP possesses the Si and phosphorus. So the EDX test of Si was performed to investigate the dispersion of SiO_2@DPP in PC. Fig. 1 shows the EDX result of PC-1 and PC-2. Here, the red dots represents the Si. It can be seen that the dispersion of Si is uniform in the PC matrix, indicating that the SiO_2@DPP particles were dispersed well in PC matrix.

2.4. Characterization

Fourier transform infrared spectroscopy (FTIR) result was recorded using a Nicolet FTIR 170SX infrared spectrophotometer (Nicolet, USA) in the wavenumber range of 500–4000 cm^{-1}.

Laser Raman spectroscopy (LRS) test was conducted on a SPEX Raman apparatus (1403, USA) at ambient temperature.

X-ray photoelectron spectroscopy (XPS) result was recorded on a XSAM80 (Kratos Co., U.K.), using Al Kα excitation radiation (hν-1486.6 eV). Before testing, the powder of sample was attached using the conductive adhesive. For the XPS data, the CasaXPS software was used to fit the XPS curves.

The dispersion of SiO_2@DPP in PC matrix was detected by an energy dispersive X-ray spectrometer (EDX, INCA PENTA-FETX3 OXFORD, USA) linked with a scanning electron microscopy (SEM, JEOL JSM-5900 LV, JEOL, Japan).

Thermogravimetric (TG) analysis was performed on a TG 209F1 (NETZSCH, Germany) thermogravimetric analyzer under a nitrogen flow at a heating rate of 10 °C/min from 40 °C to 700 °C.

The LOI test was carried out using the Oxygen Index Flammability Gauge (HC-2C, Jiangning, China) according to ASTM D 2863-97. The dimension of sheets is 130 mm × 6.5 mm × 3.2 mm.

The UL-94 vertical test was conducted using a CZF-2 instrument (Jiang Ning Analysis Instrument Company, China) according to ASTM