Polymer Degradation and Stability 98 (2013) 1022–1029

Contents lists available at SciVerse ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

# Synthesis of a novel organic-inorganic hybrid mesoporous silica and its flame retardancy application in PC/ABS

Ping Wei [a,*], Guohua Tian [b], Haizhuo Yu [a], Yong Qian [a]

[a] School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China
[b] School of Media and Design, Shanghai Jiao Tong University, Shanghai 200240, PR China

ARTICLE INFO

*Article history:*
Received 28 January 2012
Received in revised form
31 January 2013
Accepted 5 February 2013
Available online 20 February 2013

*Keywords:*
PC/ABS
Hybrid mesoporous silica
DOPO
Synergistic effect
Flame retardant

ABSTRACT

In this paper, a novel hybrid organic–inorganic mesoporous silica was synthesized through co-condensation of vinyltriethoxysilane (VTES) and tetraethyl orthosilicate (TEOS) in the presence of poly(ethylene glycol)-B-poly(propylene glycol)-B-poly(ethylene glycol) (P123) surfactants, followed by DOPO modification via the reaction between vinyl groups and P–H bond in DOPO. The mesoscopic order and pore structure of the hybrid mesoporous silica was characterized by Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), X-ray diffraction (XRD) and $N_2$ isothermal sorption. The effect of DOPO-grafted hybrid mesoporous silica (DM) and triphenyl phosphate (TPP) on the fire retardancy in polycarbonate (PC)/acrylonitrile-butadiene-styrene (ABS) was examined by limiting oxygen index (LOI), UL-94 test, thermal-gravity analysis (TGA) and cone calorimeter. Composite PC/ABS with loading of 2 wt% DM and 6 wt% TPP reached LOI value of 28% and V0 rating in UL-94 test. Present high residual weight in TGA and low heat release rate (HRR) in the cone calorimeter. It also indicated that DM is a synergistic agent with TPP, which improved the thermal stability and promoted the system giving dense char layer at high temperature.



## 1. Introduction

PC/ABS, an engineering polymer alloy, has been widely applied in various fields such as the automobile industry, electronic components, construction materials and so on [1]. Because of its easily flammability, numerous flame retarding techniques had been proposed for PC and PC/ABS [2,3].

Organophosphorous compounds are fine flame retardants for polymers, and it is usually added into PC/ABS which can also act as plasticizers [4]. Phosphoric acid triphenylester (TPP) the $OP(OC_6H_5)_3$ is one of the most frequently used phosphorus-containing flame retardants for PC and PC/ABS. Meanwhile, to obtain reasonable level of flame retardation, 10–15 phr of TPP should be added into PC/ABS depending on the PC:ABS ratio [5]. However, there are some shortcomings such as relatively low melting point, high volatilization, strictly limited its applications [6]. 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was a phosphorus-containing compound and often incorporated polymers to improve polymers' flame retardant properties and thermal stability [7,8]. It may belong to more thermal stable cyclic O=P–O chain being than the open O=P–O chain [9–11]. H. Zhong [12] synthesized a novel silicon, nitrogen, phosphorus-containing flame retardant using DOPO, and added it into PC/ABS which showed improved thermal stability and synergic effect in promoting char forming. Zhi Hu [13] prepared a novel flame retardant, which DOPO was incorporated in the molecule's backbone, and blended it with montmorillonite (MMT) in PC which reached V-0 rating and showed enhanced thermal stability with high char residual yield in combustion.

Nanoparticle fillers are highly attractive for the purpose which they can simultaneously improve the flammability and other properties of polymer nanocomposites. Bourbigot [14,15] had made progress on the research of synergistic effect of clay and zeolite 4A for polypropylene (PP) matrix containing APP/APER mixture. Hu et al. [16] investigated the thermal stability of PC/ABS/MMT nanocomposites, which showed that PC/ABS/MMT nanocomposites had higher thermal stability and lower flammability. R Zong [17] prepared PC/ABS/MMT though direct melt intercalation technique which showed significant fire performance. E. Feyz [18] studied a hybrid system of nanoclay and TPP on flame retardancy of PC/ABS, which exhibited excellent performance in the cone calorimeter and LOI test. SBA-15 is one typical mesoporous silica materials with ordered hexagonal cylinder nano-structure which had been found in extensive applications as hosting materials of catalysts, sorbents, or sensing materials [19,20]. Thus, it can be used as additive to prepare polymer nanocomposite, which the thermal stability showed significant improvement [21–23]. J. Li reported that preparation of PP/IFR system with synergistic agent SBA-15, found that addition of mesoporous materials increased the LOI value and improved the density of the residual char [24].

* Corresponding author. Tel.: +86 21 34202509; fax: +86 21 54741297.
*E-mail address:* pingwei@sjtu.edu.cn (P. Wei).

0141-3910/$ – see front matter © 2013 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.polymdegradstab.2013.02.006

Organic-inorganic hybrid mesoporous materials attracted much attention nowadays [25,26]. In this paper, hybrid mesoporous silica with high molar content of VTES precursor and DOPO modification are successfully synthesized. The ordered structure of hybrid mesoporous silica is characterized by XRD, TEM, and $N_2$ adsorption. The thermal properties and flame retardancy of PC/ABS/TPP with DOPO-grafted hybrid mesoporous silica were investigated. The synergistic effect of DM with TPP is also studied at high temperature. The aim is focused on the improved flame retardancy of PC/ABS nanocomposites and the promoting charring effect using LOI tests, UL-94 tests, TGA, cone calorimeter, scanning electron microscope (SEM) and Raman spectroscopy.

## 2. Experimental

### 2.1. Materials

TEOS, hydrochloric acid (HCl) and VTES were provided by Shanghai Chemical Reagent Co., Ltd. Pluronic P123 was provided by Aldrich. PC and ABS were provided by Yangzi Petroleum Chemical Company, China. TPP and DOPO were kindly provided by Jiangsu Yoke Technology Company, China.

### 2.2. Preparation of hybrid mesoporous silica

The synthesis of hybrid vinyl-functionalized mesoporous silica (HM) was performed according to the following procedure with a molar ratio of silane (TEOS + VTES):P123:$H_2O$:HCl of 1:0.011:214.812:6.697. First, P123 was dissolved in 1 M HCl solution. Second, TEOS was added into that solution with strong stirring at 40 °C for 2 h, VTES was added with stirring another 2 h. Then, the mixture was aged at 80 °C for 24 h without stirring. The product was filtered, followed surfactant removal by soxhlet extraction with ethanol for another 24 h. The white powder of HM was obtained after drying at 80 °C overnight.

Synthesis of DOPO-grafted hybrid mesoporous silica (DM) was carried out as follows. 6 g of HM (40 mol% VTES), 8 g of DOPO and 250 mL toluene were put into a 500 mL round-bottom flask, respectively. The mixture was then allowed to react with magnetic stirring at 110 °C under nitrogen for 8 h. The products were filtered and washed by hot ethanol several times. The final product DM was obtained by drying at 80 °C overnight.

### 2.3. Preparation of PC/ABS nanocomposites

DM, PC, ABS were dried in vacuum at 80 °C overnight before use. The proportion of PC:ABS is 4:1 by weight. Samples were melt-mixed at 205 °C in a Rheomixer TGA-7(made in Germany) as 50 g total with the desired amounts of PC/ABS, TPP and DM. The composites were hot-pressed into sheets of suitable thickness and size for tests.

### 2.4. Characterization

FT-IR measurements were performed on a Paragon 1000 spectrometer using KBr pressed pellets.

XRD patterns were recorded on a Rigaku D/Max 2000 X-ray diffractometer with a Cu Ka radiation source.

TEM images were obtained with a JEOL JEM-2100 electron microscope operating at 200 kV.

Nitrogen sorption isotherms were measured at 77 K using an ASAP 2010M + C analyzer.

TGA was determined from room temperature to 800 °C, with a heating rate of 10 °C/min in $N_2$ using a TA Q5000IR thermogravimetric analyzer.

LOI value was measured on sheets ($120 \times 6.5 \times 3$ mm$^3$) according to the standard oxygen index test ASTM D2863-77 using FTA II.

UL-94test was measured on sheets ($130 \times 12.7 \times 3$ mm$^3$) according to the American National UL-94 test ASTM D635-77.

Cone calorimeter test was carried out by Stanton Redcroft type, under a heat flux of 50 kW m$^{-2}$ according to the ASTM E-1356-90 standard.

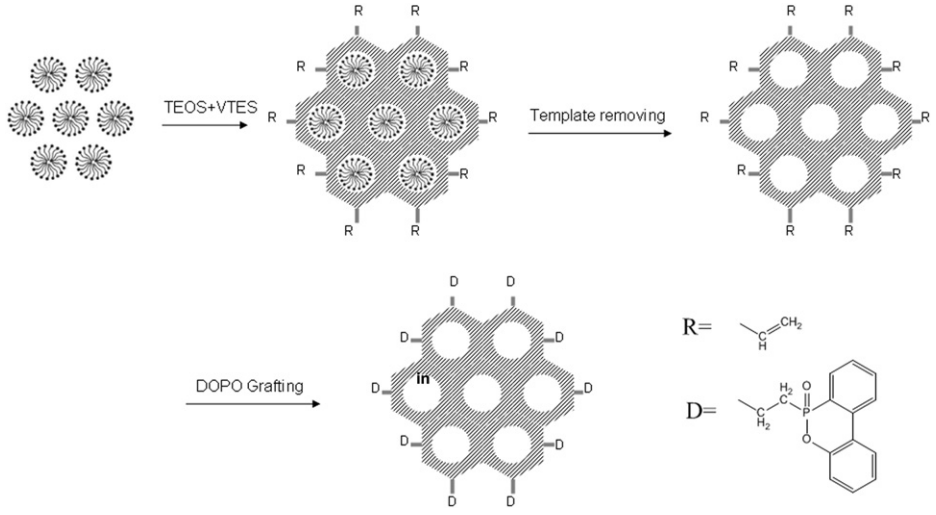
SEM micrographs of char residual were observed by S-2150(Hitachi Corp., Japan). All the samples were coated with a conductive gold layer.

Raman spectroscopy measurements were carried out at room temperature with a ThermoFisher Scientific, DXR laser Raman spectrometer with excitation provided in back-scattering geometry by a 780 nm argon laser line.

## 3. Results and discussion

### 3.1. FT-IR, XRD, TGA, TEM and $N_2$ sorption of the hybrid mesoporous silica

Scheme 1 is the synthetic route of hybrid mesoporous silica. Fig. 1 shows the FT-IR spectra of hybrid vinyl-functionalized




**Scheme 1.** Synthetic route of hybrid mesoporous silica.