



## Synergism of polysiloxane and zinc borate flame retardant polycarbonate



Sinuo Yang, Gaopeng Lv, Yuan Liu\*, Qi Wang

State Key Laboratory of Polymer Materials Engineering, Sichuan University, Polymer Research Institute of Sichuan University, Chengdu 610065, China

### ARTICLE INFO

#### Article history:

Received 1 June 2013

Received in revised form

25 September 2013

Accepted 20 October 2013

Available online 1 November 2013

#### Keywords:

Polycarbonate

Flame retardance

Polysiloxane

Zinc borate

Synergism

### ABSTRACT

Liquid polysiloxane (PSI) and zinc borate (ZB) were combined for the flame retardance of polycarbonate (PC). During polymer combustion, for the PC flame-retarded with PSI only, PSI can form char residue containing silica on the material surface. But the liquid silicone tends to drip with melting polymer and volatilize in high temperature, thus decreasing the charring performance. In the case of only ZB flame retardant involved, this inorganic flame retardant and possible some of its decomposition products ( $B_2O_3$ ) more difficultly move to the surface and it appears that they do not effectively contribute to the char formation. Present study suggests that the existing synergism between PSI and ZB is the result of chemical reaction via forming cross-linking B–O–Si structure. As results, the loss of Si/silicone is reduced by eliminating the melt dripping. Meanwhile, boron species can be “dragged” by PSI (in the form of borosiloxane) to the surface of the char residue. Consequently, Si and B elements together contribute to the integrity of char residue layer with better quality, achieving obviously improved flame retardance compared with only PSI and only ZB flame retardant systems.

© 2013 Elsevier Ltd. All rights reserved.

### 1. Introduction

Polycarbonate (PC), as an engineering plastic, has many outstanding properties including good stiffness, impact strength, transparency, dimensional and thermal stability. So it is widely applied in optical equipment, construction, automobiles, electronic devices and aeronautics, etc. It is well known that poor flame retardance is drawbacks of most polymers. Because of relatively high tendency to produce char compared with those hydrocarbon polymers, PC itself possesses self-extinguishing property and shows V-2 rating in UL-94 vertical flame test. However, higher flame retardance (V0 rating) for satisfying the requirements of electronic applications must depend on additional flame retardants loaded [1–8]. Traditional halogen-containing flame retardants exhibit high efficiency for PC, but cause environmental problems due to release of the toxic and corrosive substance during their decomposition [9–12]. By the reason, halogen flame retardants have been restricted in more and more environment protection laws and regulations. On the background, developing halogen free flame-retardant system attracts increasingly more attention [13,14].

Although halogen-free flame retardant PC or PC blend was established for decades, some efficient halogen-free flame retardants were successfully developed in recent years. Polysiloxane (PSI) was a typical one commercially used in PC. Most existing PSI flame retardants are liquid form, whose mechanism is acknowledged as that the flame retardants migrate to the material surface and produce silica char layer during combustion [15,16]. Nevertheless, PSI synthesized through complicated processes possess high cost, and moreover, only PSI generally can't achieve satisfactory flame retardancy for PC because the liquid flame retardant easily loses by dripping with the polymer melt drops before charring. In order to improve the flame retardancy, some synergists (e.g., sulfonic acid salt) are combined with PSI in formulations [17]. However, with similar high costs as well as the restriction by some regulations (perfluoroalkylsulfonic acid and carboxylic acid have been a subject of environmental and toxicity concern, e.g., perfluorosulfonate is listed in REACH regulation, but potassium perfluorobutanesulfonate used in PC is not on the candidate list of substance of very high concern (SVHC)/REACH), some sulfonic acid salts show some limitations. Therefore, seeking for a safer, cheaper and more efficient synergist combined with PSI is significant.

Zinc borate (ZB), as an inorganic flame retardant with low cost and innocuity, can release crystal water and form glassy substance on the burning material surface [18–21]. However, its large-scale applications in PC were few reported, which is attributed to the

\* Corresponding author. Tel.: +86 28 85405133; fax: +86 28 85402463.

E-mail addresses: [vinci881106@gmail.com](mailto:vinci881106@gmail.com) (Y. Liu), [qiwang@scu.edu.cn](mailto:qiwang@scu.edu.cn) (Q. Wang).

poor charring performance by individually using the flame retardant.

The combination of organic polysiloxane and inorganic ZB for the synergistic flame retardance of polymers excites the interest of researchers. For example, zinc borate has been successfully used in silicone elastomers, and polydimethylsiloxane combined with ZB was also reported to be applied in polyolefin [22]. It is believed that borosilicate may be formed during polymer combustion. Another possibility is the silica is sintered by borate to give a strong protective layer. But they have never been proven. Schartel group [23–25] investigated silicone acrylate rubber/bisphenol bis(diphenyl-phosphate) (BDP)/ZB flame retardant PC. It was found that ZnB led to a slightly enhanced PC decomposition for temperatures below 750 K, and  $Zn_3(PO_4)_2$  and borophosphate ( $BPO_4$ ) were formed in small amounts at high temperatures suggesting a reaction between BDP and ZnB during the thermal decomposition. Additionally, most of the borate was proved to be remained in the solid residues, forming an amorphous pure borate network, only 10% of boron species have protons in their environment, possibly forming the interface between a borate network and carbonaceous char.

In the research, polyphenylmethylsiloxane/ZB flame retardant PC was investigated. It revealed that the notable synergism resulted from the chemical reaction between the PSI and ZB to form B–O–Si bond. The formation of the cross-linking structure in the combustion temperature remarkably increased the system viscosity to retard the melt drips and reduced the loss of Si, and meanwhile boron element was also dragged to the surface char. As a result, more Si and B elements participated in the construction of the char layer and endowed the char with better quality, thus greatly improving the flame retardancy in the condensed phase.

## 2. Experimental

### 2.1. Materials

PSI, (polyphenylmethylsiloxane), DC8008, liquid form with a viscosity of  $22.5 \text{ mm}^2 \text{ s}$  ( $25^\circ \text{C}$ ) and specific gravity of 0.98 ( $25^\circ \text{C}$ ), was provided by Dow Corning Company.  $ZB(ZnO \cdot 3B_2O_3 \cdot 3.5H_2O)$ , powder, was purchased from Chengdu Kelong Chemical Reagent Company, China. PC pellets, 2805, was purchased from Bayer Company.

### 2.2. Sample preparation

86 wt% PC and 14 wt% flame retardants (PSI or ZB or PSI/ZB) were melt-kneaded and extruded into pellets in a twin-screw extruder with a cylinder temperature of  $230\text{--}250^\circ \text{C}$  and a screw rotation speed of 150 rpm. The obtained pellets were dried at  $120^\circ \text{C}$  for 5 h and then injection-molded into the test bars at  $260^\circ \text{C}$ .

### 2.3. Characterization

The vertical burning test (UL-94) was performed on HK-HVRA instrument according to ASTM D 3801 testing procedure with the sheet dimensions of  $125 \text{ mm} \times 13 \text{ mm} \times 1.6 \text{ mm}$ . After the flame test, the intumescent char was peeled off from the fire residues of the burned bar, and weighed to determine the charring amount.

The apparent viscosity of flame retardant PC was measured in the melting temperature ( $250^\circ \text{C}$ ) and partly decomposed temperature ( $350^\circ \text{C}$ ) of the materials by a high pressure capillary rheometer (Rosand RH7, Bohlin Instruments, UK).

MCC, FAA type, manufactured by Fire Testing Technology Limited, UK, was used to determine the heat release rate (HRR), the peak value of heat release rate (PHRR), PHRR temperature ( $T_{PHRR}$ ) and the total heat release (THR) of the materials with a heating rate of  $1^\circ \text{C/s}$  from  $75$  to  $750^\circ \text{C}$ .

The surface morphology of the fire residues was observed using a FEI QUANTA-200 (Eindhoven, Netherlands) SEM at an acceleration voltage of 15 kV. The residues were adhered to a copper plate, and then coated with gold for imaging.

XPS was recorded to determine the surface element content and their chemical combination form of the intumescent chars peeled off from the fire residues of the burned bar after UL94 test.

Inductively coupled plasma atomic emission spectrometry (IRIS Advantag 1000, manufactured by Thermo Elemental, USA) was used to measure the absolute Si and B content of the peeled intumescent proportion of the fire residues.

The intumescent proportion of the fire residues was recorded using a Nicolet 20SXB Fourier transform infrared spectrum (FT-IR).

## 3. Result and discussion

### 3.1. Flame retardancy evaluation

Two flame test methods including UL94 and MCC were used to evaluate the flame retardance of PC/PSI, PC/ZB and PC/PSI/ZB with the same flame retardant loading respectively.

From the UL94 (1.6 mm) results listed in Table 1, it can be seen that the bars of PC/ZB were almost burned to the end and hardly self-extinguished. During the combustion, a very slow charring process was observed and the average charring amount for a bar was only 0.54 g. For PC/PSI, as the liquid flame retardant can quickly migrate to the surface of the material, the charring process probably involves the reaction between the flame retardant and PC resin according to Schartel groups' research [23–25]. Consequently, the charring performance of PC/PSI was improved as compared to PC/ZB. Correspondingly, the self-extinguishment time was shortened. By contrast, PC/PSI/ZB exhibited the fastest charring speed and biggest charring amount (4.25 g), and it also possessed the shortest self-extinguishing time among the three systems, achieving V-0 rating stably. The results displayed a certain synergistic effect for PSI/ZB to promote the charring performance and improve the flame retardance. Additionally, serious melt dripping (igniting the cotton

**Table 1**  
UL94 (thickness, 1.6 mm) test results of for flame retardant PC.

Composition (%)	Average self-extinguishment time		Melt drips igniting the cotton	The observed charring process/average charring amount for a tested bar (g)	Rating
	$t_1$ (s)	$t_2$ (s)			
PC/ZB (86/14)	30	50	Yes	The slowest/0.54	NR
PC/PSI (86/14)	7	20	Yes	Medium/1.26	V-2
PC/PSI/ZB (90/4/10)	4	3	No dripping	The fastest/4.25	V-0

$t_1$  and  $t_2$ : average combustion time after the first and the second application of the flame, respectively; NR: no rating.

Download English Version:

<https://daneshyari.com/en/article/5202194>

Download Persian Version:

<https://daneshyari.com/article/5202194>

[Daneshyari.com](https://daneshyari.com)