An efficient flame retardant for silicone rubber: Preparation and application

Chen Zhu, Cong Deng[*], Jing-Yu Cao, Yu-Zhong Wang[**]

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

A B S T R A C T

An efficient flame retardant poly[N,N,N′,N′,N″,N″-hexakis-cyclotriphosphazene-[1,3,5]triazine- 2,4,6-triamine] (HPTT) was synthesized in this work, and used to flame retard silicone rubber (SR). The flame retardancy of SR/HPTT was investigated by limiting oxygen index (LOI), vertical burning test (UL-94), and cone calorimetry. At 18 wt% HPTT, the SR/HPTT composite achieved a LOI value of 31.8% and UL-94 V-0 rating, and the heat release rate (HRR), the peak of heat release rate (PHRR), and smoke production rate (SPR) were significantly reduced compared those of (neat) SR. All the flame retardation tests indicate that the flame retardancy of SR was greatly improved after incorporating 18 wt% HPTT. The flame-retardant mechanism of HPTT was investigated by thermogravimetric analysis (TGA), scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS). TGA results showed the residue of SR/HPTT was much higher than that of SR. SEM observation showed that the inner residue of SR/HPTT was more compact than that of SR. XPS further demonstrated that the Si—C, C—C, etc. structures were formed in the residue of SR/HPTT. The compact and stable char layer formed at the inner layer of the residue during thermal decomposition must be the leading reason for the excellent flame retardancy of SR/HPTT.

1. Introduction

Since the commercialization for silicone in the 40s', a variety of products have been developed around it, in which silicone rubber (SR) is the prevailing polymer due to its bio-compatibility, chemical resistance, high temperature and radiation resistance, and excellent electrical properties [1—5]. However, SR is considerably flammable [6—8]. Once being ignited, SR burns rapidly, and releases a large amount of heat, then reaches the peak of the burning intensity in a short time. The flammability of SR restricts its application in various fields. Therefore, it is important to improve the flame retardancy of SR and develop the flame-retarded SR.

The open literature and patents [9—14] show that some work on the flame retardancy of SR has been carried out. Generally, there are two approaches to flame retard SR, which are the 'additive-type' and the 'reactive-type' flame retardation [15,16], respectively.

Generally, the reactive-type flame retardation is achieved through synthesizing new intrinsic flame-retarded copolymerized SR. In this case, some problems such as high cost, complicated reaction process, environmental pollution, etc. weaken its attraction. The additive-type flame retardation can be achieved through incorporating flame retardants into polymers, which is the most economical and effective way to improve the flame retardancy of commercial polymers [17]. At present, three types of flame retardants are widely used to flame retard SR, which are platinum compounds, silicate, and metal hydroxide, respectively. Platinum or platinum compounds as a high temperature catalyst [18,19] is significantly effective in flame retarding SR, which can improve the cross-linking density and residue char of SR at only 200~600 ppm, but hardly make the SR reach the UL-94 V-0 rating in the case of no other compounds, and it will lose its flame-retardant effectiveness when contacting with P, N, S, Pb, Zn, etc. For silicates, such as mica [20—22], wollastonite [23—25] or montmorillonite [26,27], and so on, are efficient in flame retarding SR through facilitating the formation of a thick ceramic layer based on its solidification phase mechanism at a very high temperature. However, its high flame-retardant efficiency cannot be achieved at low burning temperature, so the flame-retardant efficiency of silicates is still not high. In

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

addition, both aluminum hydroxide (ATH) and magnesium hydroxide (MH) are also used to flame retard SR due to their non-toxic characteristic and smoke suppression. To meet the requirements in flame retarding SR, the high loading (>30%) for ATH or MH is necessary [8,28]. In this case, the mechanical properties of SR are seriously damaged inevitably.

As we all know, the residue left for SR is amorphous silica after burning, which is quite loose, consequently leads to the bad flame retardancy of SR due to its weak isolation as a barrier layer between material underneath and outer heating, oxygen, and combustible materials [29]. Generally, an intumenscent flame retardant can provide a barrier to the material underneath. It was confirmed that the intumenscent flame retardant containing phosphorus and nitrogen is very effective to flame retard rubber through the combined action of gas phase and condensed phase [30,31]. Generally, the organo-phosphorus molecules are very efficient radical scavengers, and the free-radical reaction corresponds to an exothermic process, so the combustion behavior is prevented [32—34]. In addition, the nitrogen-containing molecules that release gaseous byproduct can facilitate the formation of an intumescent char, which can provide thermal insulation and prevent the combustion from spreading [35—39].

Based on the highly-efficient flame retardancy of intumenscent flame retardant for SR, a chemical compound, hexachlorocyclotriphosphazene ($P_3N_3Cl_6$), was used to prepare a spirocyclic phosphazene-based intumescent flame retardant (HPTT) in this work, and the flame retardancy of SR/HPTT was investigated with the aid of LOI, UL-94, and CC tests. Moreover, the flame-retardant mechanism of HPTT was also investigated through TG, SEM, EDX, and XPS.

2. Experimental

2.1. Materials

SR (M_w, 620,000) with 0.17% vinyl, containing fumed silica (SiO_2, A-200) as reinforcement filler, was purchased from Dongjue Fine Chemicals Co., Ltd. (Nanjing, China). $N_3P_3Cl_6$ was obtained from Shanghai Yagu Chemical Co., Ltd., China, and it was purified by recrystallization from n-heptane before being used. Vulcanizing agent (DBPMH) was provided by Qiangsheng Chemical Engineering Company (Jiangsu, China).

2.2. Synthesis

The synthesis route of HPTT is shown in Scheme 1.

N,N,N′,N′,N″,N″-hexakis-hydroxymethyl-[1,3,5] triazine-2,4,6-triamine (HHTT) was synthesized in a 500 ml three-necked flask equipped with a reflux condenser, a thermometer, and a stirrer. First, both melamine (37.8 g, 0.3 mol) and 37% aqueous formaldehyde (2.6 mol, 195 g) with pH of 7.5 were added in the flask. Then, the mixture was stirred and heated until the melamine was dissolved. Here, the reaction between the melamine and the formaldehyde continued for 10 min. Next, the mixture in the flask was cooled to room temperature. After that, the resulting white solid product was filtered, washed with ethanol, and dried at 50 °C. Here, the HHTT was obtained. The melting point of the HHTT is 153 °C, and its yield is 89%.

The obtained HHTT (10 mol) was dissolved in 250 ml DMF at 40 °C, and then added into a 500 ml three-necked reaction vessel with an additional funnel, a reflux condenser, and a magnetic stirrer. The solution was maintained at room temperature, meanwhile, the $N_3P_3Cl_6$ (10 mol) dissolved in chloroform was added in the solution using additional funnel, drop by drop. Then the mixture was heated up to 40 °C, and sustained for 2 h. After that,
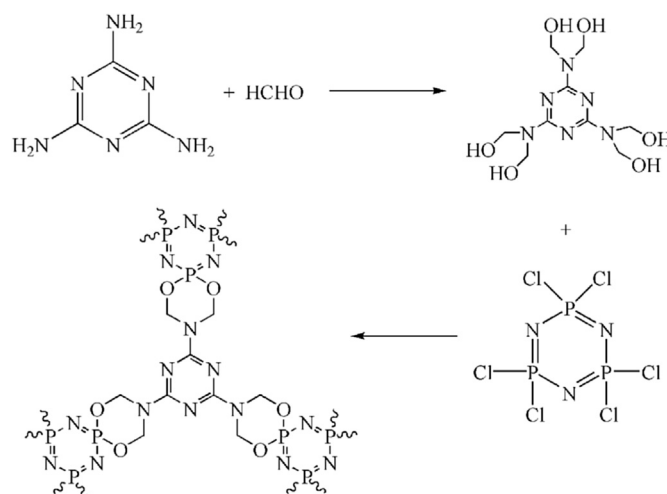
Scheme 1. The synthesis route of HPTT.

the triethylamine (60 mol) was added into the mixture. Next, the mixture was maintained at 60 °C for 4 h. When the reaction completed, the mixture solution was cooled down to room temperature, filtered, and washed with distilled water and ethanol. Finally, the powder dried to a constant weight was the intumescent flame retardant HPTT.

2.3. Sample preparation

All the samples (Table 1) were prepared using a two-roll mixer (XK-160, Kechuang rubber and plastic machinery co., Shanghai, China) at room temperature. The preparation process is described as follows. The SR was mixed in the two-roll mixer until it became soft, then all fillers were incorporated in the soft SR during mixing to obtain a homogeneous batch. Next, the vulcanizing agent was added, and the mixing time lasted for about 10 min. After that, the resulting mixture was compressed into sheets with the thickness of 3.2 mm or 1 mm, respectively, accompanied by the vulcanizing of all samples.

2.4. Measurement

The Fourier transform infrared spectroscopy (FTIR) spectra were recorded by a Nicolet FTIR 170 SX spectrometer (Nicolet, America) using the KBr disk, and the wave number range was set from 4000 to 500 cm^{-1}.

The contents of carbon (C), nitrogen (N), and hydrogen (H) in HPTT were measured by elemental analysis (EA) on CARLO ERBA1106 instrument (Carlo Erba, Italy).

The actual phosphorus contents of the purified samples were determined by oxygen flask combustion-inductively coupled plasma atomic emission spectroscopy (ICP-AES) method.

Energy dispersive X-ray (EDX) measurements were conducted on an energy dispersive X-ray spectrometer (EDX, INCA, PENTA-FETX3, OXFORD) equipped with an SEM (JEOL JSM-5900LV).

Tensile test was performed on a Universal Testing Machine DCS-5000 (Shimadzu, Japan) with a constant speed of 200 mm/min at room temperature. All measurements were repeated five times, and the mechanical properties results were from the average values.

The TGA was performed using an SDT Q600 thermal analyzer instrument under N_2 flow of 50 mL/min. The specimens (about 3 mg) were heated from room temperature to 700 °C at a heating