Polymer Degradation and Stability 99 (2014) 43–52

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

# Synthesis of a novel dicyclic silicon-/phosphorus hybrid and its performance on flame retardancy of epoxy resin

Shiqiang Song, Jiajun Ma, Ke Cao, Guanjun Chang, Yawen Huang*, Junxiao Yang*

*State Key Laboratory Cultivation Base for Nonmetal Composite and Functional Materials & School of Material Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, People's Republic of China*

ARTICLE INFO

*Article history:*
Received 8 March 2013
Received in revised form
28 October 2013
Accepted 7 December 2013
Available online 16 December 2013

*Keywords:*
Epoxy resin
Flame retardancy
Silicon-/phosphorus hybrid
Condensation polymerization

ABSTRACT

A novel silicon-/phosphorus hybrid (SDPS) was synthesized by a condensation polymerization of diphenylhydroxysilane and spirocyclic pentaerythritol di(phosphate monochloride). The use of SDPS and the cooperative use of SDPS with P–N hybrid in flame retardant epoxy resin (EP) were investigated. Limiting oxygen index and cone calorimeter tests showed that the loading of SDPS and the cooperative use of SDPS and P–N hybrid in EP provided enhanced fire resistance. TGA, TG-FTIR and SEM measurements revealed that the enhancement in fire resistance was arising from the formation of a compact honeycomb carbonaceous structure hybridized by silica, the good char forming ability and the inhibition of flammable gas release. Further analysis from Raman spectra revealed that the compact carbonaceous layer may be originated from an increase in ordering of amorphous carbonaceous layer.



## 1. Introduction

Epoxy resins are globally used on a large scale for microelectronics packaging materials, biotechnology, mechanical engineering and environment engineering, owing to their excellent moisture, solvent and chemical resistances, low shrinkage on cure, toughness, high adhesion to many substrates and superior electrical resistance property [1,2]. Flame-retardant treatment of epoxy resins by introducing halogens (mainly Cl and Br) was most widely used. However, the uses of halogen-containing additives are evoking the environment issue as they produce toxic gases such as dioxine and furane, during their combustion [3]. Recently, some ecological and friendly flame retardants have been developed to improving burning resistance of epoxy resins, involving natural mineral (montmorillonite, kaolinite, aluminum hydroxide et al.) [4,5], phosphorous-, nitrogen-, boracium- and silicon-containing compounds [6–8].

Phosphorus-containing compounds have shown promising application as halogen-free, flame retardants in epoxy resins [9–11]. On one hand, phosphorus-containing compounds can hindrance combusting of H or OH·, thus reducing the energy of flame in the gas phase. On the other hand, they generally convert into polyphosphoric acid in the solid phase during decomposition, consequently catalyzing the formation of a protective carbonaceous layer, which is highly thermal stability and can retard further decomposition of polymer chains. Moreover, research about the flame retardancy of epoxy resins has shown a high independency on the phosphorus contents. Increase of phosphorus contents can effectively improve the flame retardancy of resins. However, high loading of additive-type phosphorus-containing compounds destroyed the mechanical properties and the thermal stability and led to outflow phenomenon, further lowering the efficiency of the flame retardant. Thus, phosphorus/nitrogen combined systems have been developed. Most of these systems are based on phosphorus-/nitrogen-containing compounds, such as ammonium polyphosphate (APP), and melamine phosphate (MP). In addition, these compounds were commonly used in assistance with polyatomic alcohol like pentaerythritol (PER), consequently constructing intumescent flame retardation (IFR) composed by a blowing agent, a carbonization agent, and an acid source.

Silicon-containing compounds have also aroused much attention [12,13]. Compared with phosphorus/nitrogen containing compounds, silicon-containing compounds are regarded as an environmentally friendly flame retardant. More importantly, they could migrate to the surface of polymer matrix at high temperature due to their low surface energy, forming a protective silica layer to hamper the penetration of air and heat into polymers. However, some studies have shown that silicone-containing compounds [14,15], e.g., polydimethylsiloxanes (PDMS), show unsatisfied flame retardancy.

* Corresponding authors. Tel./fax: +86 816 2419076.
*E-mail addresses:* huangyawen@swust.edu.cn (Y. Huang), yangjunxiao@swust.edu.cn (J. Yang).

0141-3910/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymdegradstab.2013.12.013

In recent years, the P and Si combined system have been intensively investigated and presented highly improved flame retardancy [16–26]. For example, Schartel et al. reported a P and Si combined flame retardant by cooperatively using Si-based and P-based FR. The fire retardancy in PC composites was caused by both flame inhibition in the gas phase and inorganic-cabonaceous residue formation in the condensed phase [16–20]. Chen et al. reported a new flame retardant containing silicon and caged bicyclic phosphate for polyamide 6. The condensed phase action was considered as the major flame retardancy mechanism with the fuel reduction action as the minor [21]. In the study of Sponton et al., silicon-based and phosphorus-based compounds were directly incorporated into the chemical structure of polybenzoxazines to enhance the flame retardancy. The fire retardancy mechanism was described as that silicon provides an enhancement of the thermal stability of the char [22]. Yang et al. synthesized a novel P/Si hybrid FR (DOPO-POSS). Its use in epoxy resin, polyamide and polycarbonate were investigated, respectively. An interesting blowing-out effect or synergistic effect of P/Si were reported [23–25]. Overall, most current P and Si combined systems generally involved the blends of P-based and Si-based FRs or small molecular P/Si hybridized system. Polymeric P/Si hybridized systems, whose P-based and Si-based moieties were linked by chemical bonds, were seldom reported. Compared with conventional P/Si-combined systems, P/Si hybridized polymeric structures would show some special flame retardant properties. First, polymeric structures enabled chain entangling and chain folding, consequently leading to high local concentration of phosphorus-related acidic catalysts and possibly facilitating the char formation. Second, the P-based units were linked with Si-based units by relatively weak P–O–Si bonds, whose scission simultaneously produced active P and Si-containing moieties. As a consequence, the phosphorous catalyzed char forming and the silica forming processes may tend to take place synchronously. This may be helpful to enhance the barrier effect of charring layers.

In this work, a novel silicon-/phosphorus-containing flame retardant (SDPS) was synthesized by condensation polymerization of diphenylhydroxysilane and spirocyclic pentaerythritol di(phosphate monochloride) (SPDPC). This new flame retardant is characteristic of polymeric structure with P–O–Si linkages in mainchains. To construct an intumescent system, SDPS was cooperatively used with mono (4, 6-diamino-1,3,5-triazin-2-aminium) mono (2,4,8,10-tetraoxa-3,9-di-phosphaspiro [5.5] undecane-3, 9-bis (olate) 3, 9-dioxide) (SPDM), which was a well-established P–N intumescent flame retardant. The flame retardancy performance of epoxy resin/SDPS and epoxy resin/SDPS/SPDM composites were evaluated by LOI and cone calorimeter tests. Thermal decomposition property, char residue structure and morphology, gas evolution of epoxy resin composites has been characterized by TGA, FTIR/EDS, SEM, Raman and TG-FTIR, respectively. Finally, the flame retarding mechanism was investigated.

## 2. Experimental

### 2.1. Materials

Phosphorus oxychloride ($POCl_3$), Pentaerythritol (PER), tripolycyanamide (MA), triethanolamine (TEOA) and other common solvents (Chengdu Kelong Reagent Co.) were purified with standard methods before used unless noted otherwise. Diphenyldichlorosilane (China Bluestar Chengrand Chemical Co.), Methyl hexahydrophthalic anhydride (MHHPA, Puyang Huicheng Chemical Co.), Epoxy resin, diglycidyl ether of biphenol A, DEGBA, with epoxy value of 0.4083 mol/100 g (Lanzhou Bluestar Resin Co.) were used without further purification. Diphenylsilanediol (DPSD) was synthesized via the method reported by Burkhard [18].

### 2.2. Synthesis of 3, 9-dichloro-2, 4, 8, 10-tetraoxa-3, 9-diphosphaspiro [5. 5] undecane 3, 9-dioxide (SPDPC) [19]

In a 1000 mL glass flask equipped with a magnetic stirrer, a thermometer, a circumference condenser and heating bath, pentaerythritol (PER) (1.0 mol) and phosphorus oxychloride ($POCl_3$) (11.0 mol) were mixed at room temperature. Then, the temperature was elevated slowly to 105–110 °C. The reaction was conducted for more than 20 h until HCl was not eluted. The raw product was filtered and washed by dichloromethane ($CH_2Cl_2$), tetrachloromethane ($CCl_4$) and ether sequentially. The product was dried to constant weight at 50 °C in vacuum oven, producing a white solid powder (yield: 82%).

### 2.3. 3-((Methoxydiphenylsilyl) oxy)-9-methyl-2, 4, 8, 10-tetraoxa-3, 9-diphosphaspiro [5. 5] undecane 3, 9-dioxide (SDPS)

SPDPC (29.7 g, 0.1 mol) were added in a 250 mL glass flask and dispersed by acetonitrile (100 mL) at room temperature, and then the temperature was elevated to 80 °C slowly. When SPDPC was fully dissolved, diphenylsilanediol (DPSD) (20.7 g, 0.15 mol) was added to the solution at once. The reaction was conducted at 80–85 °C for 18 h under stirring and $N_2$ environment. The solution was charged into ethanol, producing a white solid power. The white solid powder was washed with ethanol and ether sequentially, and then dried to constant weight at 50 °C in vacuum oven.

### 2.4. Mono (4, 6-diamino-1, 3, 5-triazin-2-aminium) (2, 4, 8, 10-tetraoxa-3, 9-diphosphaspiro [5. 5] undecane-3, 9-bis (olate) 3, 9-dioxide) (SPDM) [27]

In a 250 mL glass flask, SPDPC (14.9 g, 0.05 mol), tripolycyanamide (12.6 g, 0.1 mol) and deionized water (125 mL) were mixed at room temperature in $N_2$ environment. Then the temperature was elevated to 100 °C slowly and kept for more than 15 min. Resultant solution was allowed for cooling at room temperature to produce precipitates. The precipitates were washed with cold water for several times and then dried to constant weight at 50 °C in vacuum oven, producing a white solid power. FTIR data: 3412 $cm^{-1}$ ($NH_2$), 1618 and 1515 $cm^{-1}$ (C=N), 1255 $cm^{-1}$ (P=O) and 1025 $cm^{-1}$ (P–O); $^1H$ NMR data: 7.4 ppm ($PO_3$–$H^+$), 3.9 ppm ($NH_2$), 3.4 ppm ($CH_2$); $^{13}C$ NMR data: 160.1 ppm (C=N), 67.8 ppm (PO–C), 35.4 ppm (C*-C4).

### 2.5. Preparation of epoxy composites

Epoxy resin (EP) and flame retardants (5.5 wt. % or 10.4 wt. % of epoxy resin) were added into a three-necked flask equipped with a mechanical stirrer. The mixture was heated at 90 °C until flame retardant was completely disperse in EP to form homogeneous system. Then curing agent, methyl hexahydrophthalic anhydride (MHHPA, 68.8 wt. % of EP) and accelerating agent, triethanolamine (TEOA, 2.0 wt. % of EP), were added sequentially. The reaction mixtures were pre-cured in a mould at 100 °C for 1 h, followed by a final curing at 120 °C for another 2 h, giving rise to pellet solid resins.

### 2.6. Characterization

Fourier transform infrared (FTIR) spectra were obtained on a Perkin Elmer Spectrum One spectrophotometer with a resolution of 2 $cm^{-1}$. Raman spectroscopy was recorded on Via-Reflex confocal laser Raman spectrometer (Renishaw Ltd) with a resolution of 2 $cm^{-1}$. $^1H$ and $^{13}C$ NMR spectra were collected on a Bruker Acance spectrometer (400 MHz) using tetramethylsilane (TMS) as internal reference and deuterated dimethyl sulfoxide (DMSO-$d_6$) as solvent.