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Combustion and thermal properties of epoxy/phenyltrisilanol polyhedral oligomeric silsesquioxane nanocomposites

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Abstract Organic–inorganic hybrid composites of epoxy and phenyltrisilanol polyhedral oligomeric silsesquioxane ($Ph_7Si_7O_9(OH)_3$, POSS-triol) were prepared via in situ polymerization of epoxy monomers. The nanocomposites of epoxy with POSS-triol can be prepared in the presence of metal complex latent catalyst, aluminum triacetylacetonate ([Al]) for the reaction between POSS-triol and diglycidyl ether of bisphenol A (DGEBA). The dispersion morphology of organic–inorganic hybrid was characterized by scanning electronic microscopy (SEM). The thermostability of composites was evaluated by thermal gravimetric (TG) analysis. The flammability was evaluated by cone calorimeter test. The presence of [Al] latent catalyst leads to a decrease in combustion rate with respect to epoxy and epoxy/POSS composites as well as reduction in smoke, CO and CO_2 production rate. The effect of [Al] is to reduce the size of spherical POSS particles from 3–5 μm in epoxy/POSS to 0.5 μm in epoxy/POSS[Al]. Furthermore, POSS with smaller size may form compact and continue char layer on the surface of composites more efficiently.

Keywords Polyhedral oligomeric silsesquioxane · Flame retardancy · Latent catalyst · Cone calorimeter

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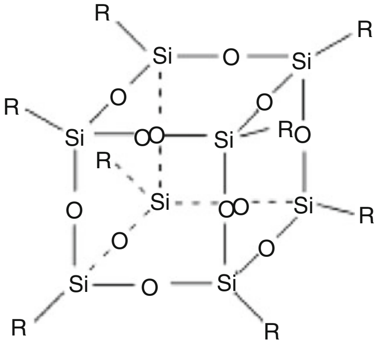
Introduction

Epoxy is one of the most commonly used matrix materials for engineering applications of fiber-reinforced polymeric composites because of their excellent engineering performance and ease of processing. However, based on more stringent regulatory requirements, its application is limited due to its flammability. Halogen-containing compounds are commonly applied as flame retardants in epoxy resins and exhibit excellent flame-retardant performance, but because of their toxic gas emissions are becoming much less favored [1].

Organic–inorganic hybrids with nano-scale structures have undergone a significant evolution because of their exceptional properties when compared with basic polymers [2–5]. An improvement in flame-resistant properties of polymers has been obtained with nano-scale additives. Most efforts have been dedicated to the development of layered silicates, layered double hydroxides, and carbon nanotubes/polymer nanocomposites [6–15]. The main proposed mechanism of fire retardancy of nanocomposites involves the formation of an insulating char, which reduces the amount of combustible volatile products available for burning in the gas phase.

Polyhedral oligomeric silsesquioxane (POSS) reagents, monomer, and polymer are a new chemical for preparing nanoreinforced organic–inorganic hybrids with enhancement of the properties in polymers. POSS consists the structure of cube-octameric frameworks represented by the formula ($R_8Si_8O_{12}$) with an inorganic silica-like core (Si_8O_{12}) surrounded by eight organic corner groups, one or more of which is reactive or polymerizable (Scheme 1). POSS are recognized to be the ceramic precursor compounds which explaining their excellent oxidation resistance and fire retardancy [16, 17].



Scheme 1 Structure of a completely condensed polyhedral oligomeric silsesquioxane (POSS)

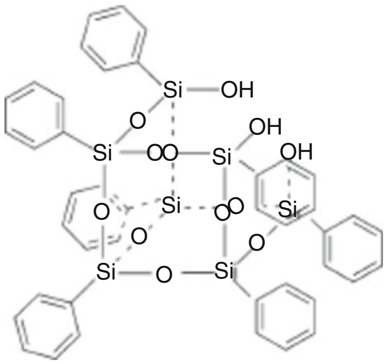
Bourbigot et al. studied polyurethane/POSS nanocomposites as flame-retarded coating for polyester and cotton fabrics on a cone calorimeter. Two different POSSs, poly (vinyl silsesquioxane) resin and octamethyl-POSS, were used in their study. PU/POSS nanocomposite coating with poly(vinyl silsesquioxane) resulted in 50% reduction of the heat release rate (HRR) peak, whereas octamethyl-POSS did not show any improvement in fire retardancy [18].

Thermal mechanical properties and thermal stability of epoxy networks modified by multifunctional polyhedral oligomeric silsesquioxanes (POSS)-containing amine groups or epoxy groups were also studied by the means of differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis [19–21].

PP/POSS, PS/POSS, and PMMA/POSS composites were also studied by the means of cone calorimeter tests [22–24]. Both PP/POSS and PS/POSS composites showed an improvement in fire retardancy; however, PMMA/POSS did not show any improvements with respect to neat PMMA. For PP/POSS composites, the contribution in fire retardancy was attributed to the catalytic effect of Al leading to partial PP charring, and the dispersion of nanofiller on submicron scale would also lead to higher fire retardancy.

Since the key for polymeric nanocomposites with exceptional properties when compared with traditional polymeric composites is the nano-scale structure, nanodispersion versus micro-dispersion is one of the key factors in making a flame-retarded polymer [25, 26].

In this study, the effect of POSS dispersion in epoxy/phenyltrisilanol POSS (POSS-triol, Scheme 2) composites has been modified with the assistance of a metal complex aluminum triacetylacetonate. The objective of this article is to understand the effect of dispersion of POSS reagents in the matrix on flame retardancy.



Scheme 2 Structure of phenyltrisilanol polyhedral oligomeric silsesquioxane (POSS-triol)

Experimental

Materials

An epoxy resin was used in this study, diglycidyl ether of bisphenol A (DGEBA, D.E.R. 332, Dow Chemical, equivalent epoxide [E] weight: 173). The epoxy was cured with diethylene toluene diamine (DETDA, EPI-CURE W, Miller-Stephenson chemical company, Inc.). Phenyltrisilanol (denoted POSS-triol) (Scheme 2) polyhedral oligomeric silsesquioxanes was purchased from Hybrid Plastics, CA. The aluminum triacetylacetonate and tetrahydrofuran (THF) were purchased from Sigma–Aldrich. All the materials were used as received.

Samples preparation

The preparation of hybrid composites was based on the preparation reported by Liu et al. [27]. Briefly, the desired amount of POSS-triol (10 wt%) was added to the epoxy resin. The mixture was stirred at 50 °C until a homogeneous solution was obtained. For the formulation of reaction with the latent catalyst aluminum triacetylacetonate (0.6 wt% of DGEBA) solution in THF was added at 120 °C with vigorous stirring for 30 min, and finally the stoichiometric EPI-CURE W was added to the above mixtures. The resulting mixture was cast in the mold and cured at 121 °C for 2 h and at 177 °C for an additional 2 h and finally cooled to ambient temperature. Neat epoxy was processed in the same condition as a reference material.

Instrument methods

Cone calorimetry test

Combustion tests were performed with a Cone Calorimeter; using 100 × 100 × 3 mm^3 specimens in the standardized cone calorimeter procedure (ASTM E-1354-02d). The tests were performed at 35 kW m^{-2} external heat flux, to evaluate the fire properties of the composites in conditions comparable to a mild fire scenario [28]; three tests for each sample were measured.

Microscopy

To investigate the morphology of POSS-containing epoxy hybrids, the samples were fractured under cryogenic condition using liquid nitrogen. The fracture surfaces were coated with thin layers of gold–palladium. Residues after burning were observed. All specimens were examined with a JEOL JSM-7401F field-emission scanning electron microscope.

Thermogravimetric analysis

Thermogravimetric analyses were performed on a Q 50 thermogravimetric analyzer from TA instruments with a heating ramp of 10 °C min^{-1} from 50 to 800 °C under air atmosphere.

Results and discussion

Morphology of hybrid composites

Phenyltrisilanol POSS (POSS-triol) can be the homogeneous and transparent mixtures with DGEBA and DETDA at 50 °C. It was observed that initially the transparent epoxy/POSS mixture was cloudy after curing. However, after a small amount of aluminum triacetylacetonate ([Al]) was added to the mixture, the resulting composites were much more transparent. The SEM images of dispersion of POSS in epoxy matrix are shown in Fig. 1. The spherical particles of POSS were uniformly dispersed in the epoxy matrix. The difference between epoxy/POSS and epoxy/POSS[Al] hybrid composites was the sizes of the POSS particles. It has been noted that the presence of the latent catalyst [Al] decreased the size of the POSS particles from 5 μm in epoxy/POSS composites to around 0.5 μm in epoxy/POSS [Al] composites at the same loading (10 wt%). The present of aluminum triacetylacetonate ([Al]) acted as a catalyst to accelerate the reaction of DGEBA with POSS-triol [27]. The dispersion to a submicron scale would probably further enhance the combustion behavior of composites.

Thermal degradation and thermal oxidation of epoxy/POSS composites

The thermal stability of the epoxy, epoxy/POSS, and epoxy/POSS [Al] hybrid composites was measured with TG (Fig. 2). The patterns of the thermogravimetric curves of the epoxy composites with POSS were similar to the patterns of the control resin, which meant the thermal mass loss of the composites was coming from the epoxy resin portion. The thermo-degradation of the epoxy and its composites took place in two steps. First, degradation was observed between 350 and 450 °C with production of alkyl group species from polymer backbone and formation carbonaceous compounds, which was working as physical barrier to protect substrates from fire via reducing the energy and mass transfer between substrates and heat source (fire). In the second step (between 450 and 600 °C), the carbonaceous compounds were oxidized and volatilized. Therefore, the thermo-oxidation stability of carbonaceous compounds formed between 350 and 450 °C

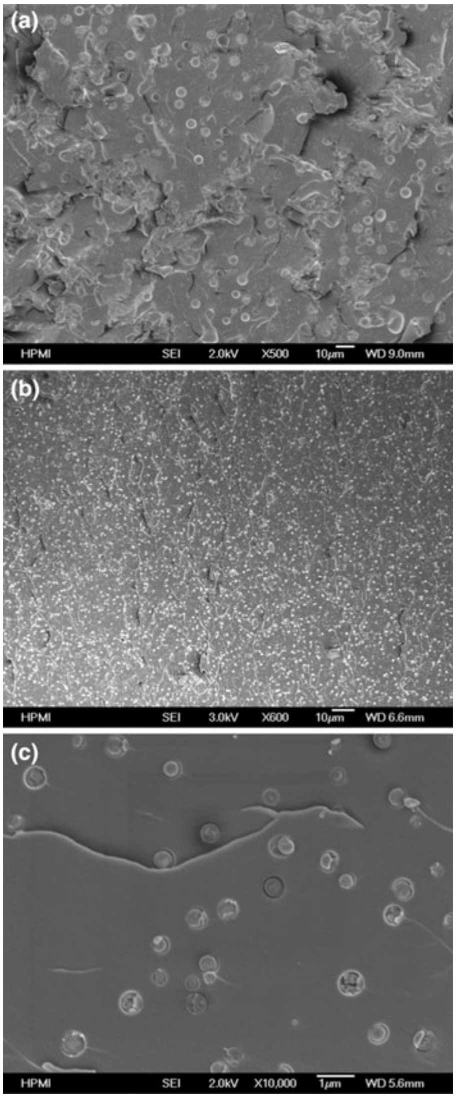


Fig. 1 SEM micrographs of the hybrid composites cured with or without [Al]. **a** Epoxy/POSS, **b** epoxy/POSS[Al], and **c** higher magnification of **b**

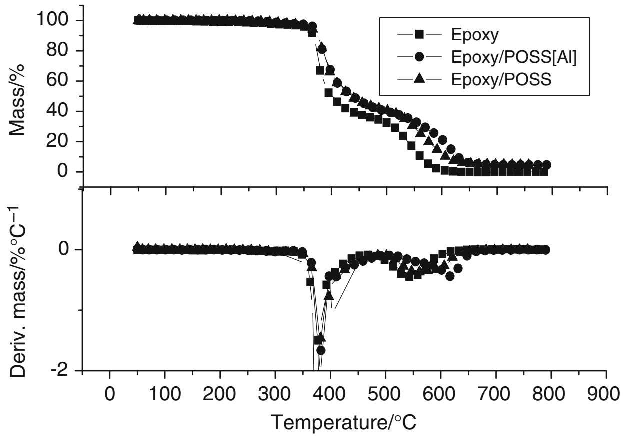


Fig. 2 The thermal gravimetric analysis results of epoxy, epoxy/POSS, and epoxy/POSS[Al] composites in air

played the main effect on flame resistance of the composite materials. Based on the DTG curves, the temperatures of maximum mass loss (T_{max}) of the epoxy/POSS composites shifted toward high temperature and the epoxy/POSS[Al] showed the highest T_{max}. Since the second stage of mass loss of an epoxy resin in air was related to the oxidation of the residual formed from thermal decomposition of the resin, the nano-additives acted as a thermal insulating material to the residual, because of their excellent oxidation resistance and reaction to fire. The high char yields also implied that relatively small amounts of volatile small molecules were released under thermal decomposition. The presence of [Al] also improved the thermal stability of carbonaceous compounds formed during combustion.

Combustion behavior of epoxy/POSS composites

Cone calorimeter is one of the most effective bench-scale methods to study the inflammabilities of materials. The main parameters obtained from cone calorimeter measurements were reported in Table 1 for each material, including time to ignition (TTI), HRR, peak HRR, CO and CO_2 yield, and mass loss during combustion, etc., among which HRR especially peak HRR was regarded as the most important parameters. Figure 3 shows the HRR results. There are two peaks in the heat-release curves, which are comparable with TG results. Under external heat flux, the samples' surface was burning and releasing heat until first peak. The carbonaceous compound was formed and left as a layer on the top of the samples. The carbonaceous layer acted as a barrier reducing the flammable components and heat release. The carbonaceous layer was oxidized and decomposed in the external heat flux. The more flammable components that were released from carbonaceous layer feeding the fire, the more heat released, which was related to the second peak in the heat-release curve. As compared to control epoxy sample, the addition of POSS reduced the peak HRR of epoxy from 883 to 777 kW m^{-2}, but did not show the reduction of the second peak HRR. However, epoxy/POSS[Al] sample has lower peak release rate (590 kW m^{-2}) and the second peak HRR disappeared. This was explained by the addition of POSS in epoxy/POSS because it accelerates the char formation resulting in the reduction of the HRR, but the thermal stability of the char was not enough to resist the thermo-oxidation. However, the presence of [Al] may help char formation more efficient and thermo-stable than that of the other two samples.

Smoke is another killer in the fire hazard. Smoke production rate (SPR) curves are shown in Fig. 4. The results show that the epoxy/POSS[Al] had the lowest SPR and

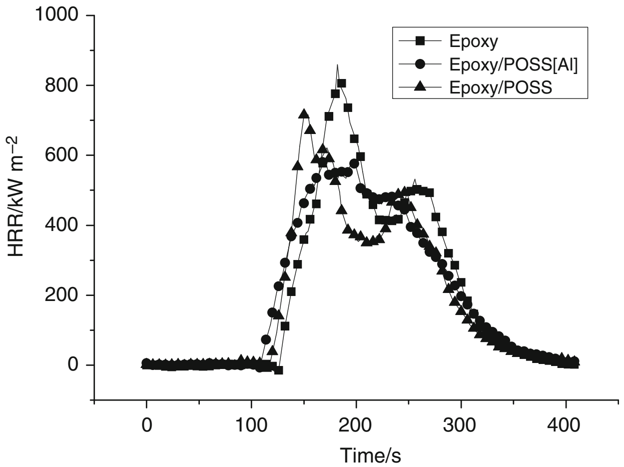


Fig. 3 The HRR results of epoxy, epoxy/POSS, and epoxy/POSS[Al] composites

Table 1 Main parameters from cone calorimeter measurements

	TTI/s	Peak HRR/kW m^{-2}	Total heat release/MJ m^{-2}	Total smoke released
Epoxy	124	883	86.2	4108.3
Epoxy/POSS[Al]	106	590	80.7	3550.0
Epoxy/POSS	114	777	81.0	3586.9

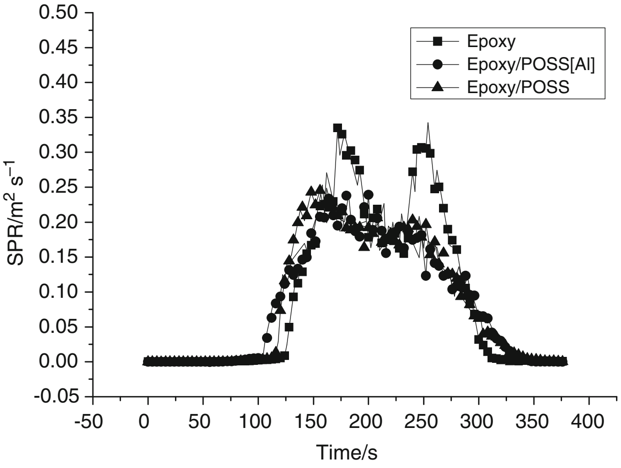


Fig. 4 Smoke production during combustion of epoxy, epoxy/POSS, and epoxy/POSS[Al]

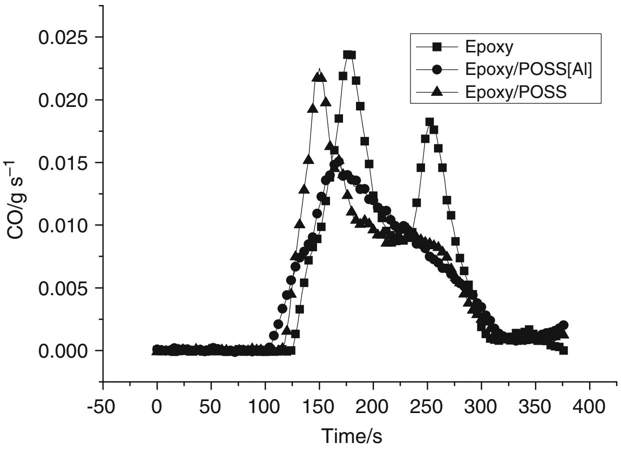


Fig. 5 CO concentration in the combustion of epoxy, epoxy/POSS, and epoxy/POSS[Al]

total smoke yield (Table 1). The lower smoke production was related to the more aromatic specimen left in the carbonaceous layer, which led to higher char yield.

The CO and CO_2 released in the combustion are shown in Figs. 5 and 6. The shape of CO- and CO_2-release curve was similar to the HRR curves. The second CO- and CO_2-release peak in the curve of epoxy/POSS decreased in the combustion. Moreover, a significant decrease in CO and CO_2 yield was found in the sample epoxy/POSS[Al]. These enhancements on reducing toxic character in the combustion properties improved the fire safety performance.

In the mass loss and mass loss rate curves obtained in the combustion course (Fig. 7). The lowest mass loss rate was clearly observable for epoxy/POSS[Al], which means that it had the higher char yield of composite after combustion.

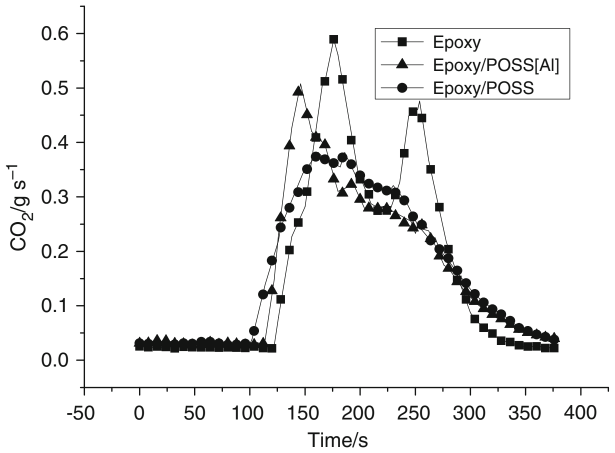


Fig. 6 CO_2 concentration in the combustion of epoxy, epoxy/POSS, and epoxy/POSS[Al]

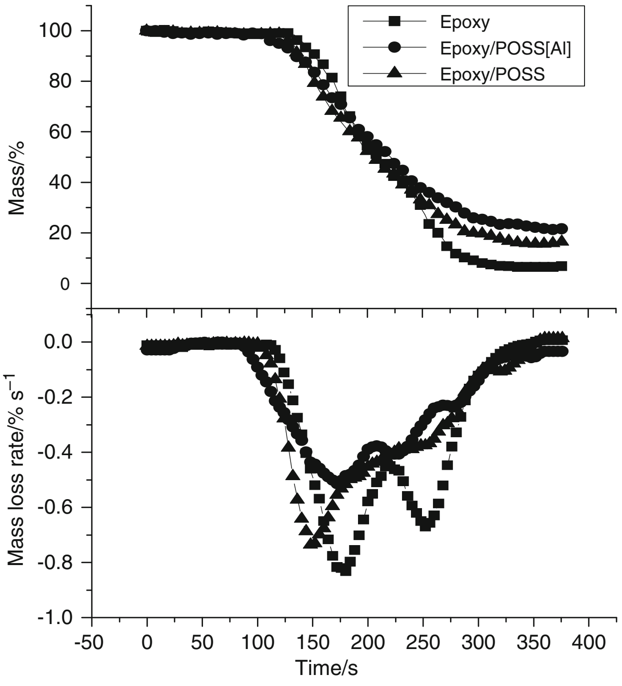


Fig. 7 Mass curves during combustion (*top*) mass (*bottom*) mass loss rate

SEM images of residues of epoxy/POSS composites

The morphology of carbonaceous residue is shown in Fig. 8. After burning, the epoxy/POSS[Al] left a compact, uniform char layer, however, there were a lot of holes on the carbonaceous residue left by epoxy/POSS, which gave the positive evidence that the char layer of epoxy/POSS[Al] formed during combustion acted as barrier more effectively than the char from epoxy/POSS. The

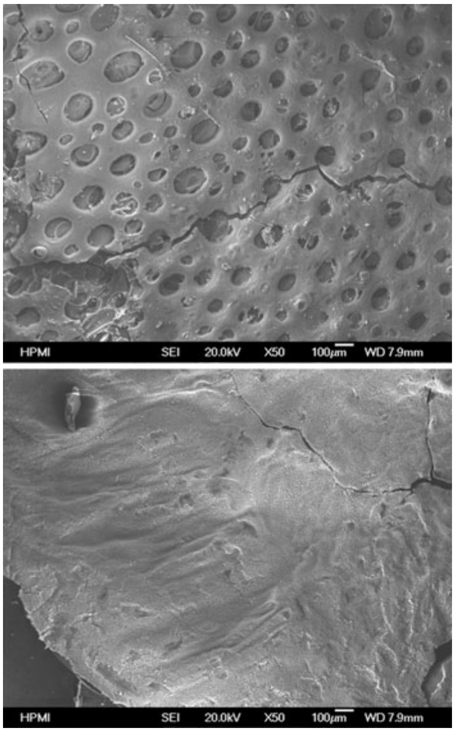


Fig. 8 SEM micrograph of residues from epoxy/POSS (*up*) and epoxy/POSS[Al] (*down*)

morphology of residue may be related to the sizes of the POSS particles dispersed in matrix. The smaller size of particle meant a higher surface area to volume aspect ratio. During combustion, the small POSS particles with higher surface area decomposed and formed an insulating char faster than the big POSS particles. In the case of epoxy/POSS[Al], the insulating char formed quickly during combustion. However, the size of POSS particles in epoxy/POSS was so big that the surface coverage was low; therefore, the formation rate of fire retardant char was not efficient and a continuous char layer could not be formed during combustion.

Conclusions

Organic–inorganic epoxy/POSS nanocomposites were prepared with the latent catalyst aluminum triacetylacetonate. The presence of [Al] complex could reduce the particle size of POSS from micron scale to submicron scale in the epoxy matrix and improve the fire retardant properties. The thermostability of composites was evaluated by thermal gravimetric (TG) analysis. For epoxy-containing POSS, when compared with epoxy, incorporating POSS into epoxy resins alters degradation characteristics, which decreases mass loss and increases the char yield and $T_{\max}$. The flammability was evaluated by cone calorimeter test. The presence of [Al] latent catalyst leads to a decrease in combustion rate with respect to epoxy and epoxy/POSS composites as well as reduction in smoke, CO, and CO_2 production rate. The possible mechanism of these improvements could be deduced as following: in the same amounts, the smaller particle size of POSS dispersed in epoxy meant the more area coverage of POSS particles, which led to the higher efficiency in forming insulating char on the surface of composites during combustion. The carbonaceous char obtained at the end of combustion shows compact structure, giving the positive evidence.

References

1. Lu SY, Hamerton I. Recent developments in the chemistry of halogen free flame retardant polymers. Prog Polym Sci. 2002;27:1661–712.
2. Whitesides GM, Mathias TP, Seto CT. Molecular self-assembly and nanochemistry: a chemical strategy for the synthesis of nanostructures. Science. 1991;254:1312–9.
3. Lan T, kaviratan PD, Pinnavaia TJ. Mechanism of clay tactoid exfoliation in epoxy–clay nanocomposites. Chem Mater. 1995; 7:2144–50.
4. Giannelis EP, Krishnamoorti R, Manias E. Polymer-silicate nanocomposites: model systems for confined polymers and polymer brushes. Adv Polym Sci. 1999;138:107–47.
5. Schwab JJ, Lichtenhan JD. Polyhedral oligomeric silsesquioxane (POSS)-based polymers. Appl Organomet Chem. 1998;12: 707–13.
6. Zammarano M, Franceschi M, Bellayer S, et al. Preparation and flame resistance properties of revolutionary self-extinguishing epoxy nanocomposites based on layered double hydroxides. Polymer. 2005;46(22):9314–28.
7. Kashiwagi T, Grulke E, Hilding J, et al. Thermal and flammability properties of polypropylene/carbon nanotube nanocomposites. Polymer. 2004;45(12):4227–39.
8. Kashiwagi T, Du FM, Douglas JF, et al. Nanoparticle networks reduce the flammability of polymer nanocomposites. Nat Mater. 2005;4(12):928–33.
9. Gilman JW. Flammability and thermal stability studies of polymer layered-silicate (clay) nanocomposites. Appl Clay Sci. 1999;15:31–49.
10. Gilman JW, Jackson CL, Morgan AB, Harris R Jr, Manias E, Giannelis EP, et al. Flammability properties of polymer-layered-silicate nanocomposites polypropylene and polystyrene nanocomposites. Chem Mater. 2000;12:1866–73.
11. Zanetti M, Camino G, Mülhaupt R. Combustion behaviour of EVA/fluorohectorite nanocomposites. Polym Degrad Stab. 2001;74:413–7.
12. Zhu J, Uhl FM, Morgan AB, Wilkie CA. Studies on the mechanism by which the formation of nano-composites enhances thermal stability. Chem Mater. 2001;13:4649–54.
13. Zhu J, Start P, Mauritz A, Wilkie CA. Thermal stability and flame retardancy of PMMA-clay nanocomposites. Polym Degrad Stab. 2002;77:253–8.
14. Morgan AB, Harris RH Jr, Kashiwagi T, Chyall LJ, Gilman JW. Flammability of polystyrene layered silicate (clay) nanocomposites: Carbonaceous char formation. Fire Mater. 2002;26: 247–53.
15. Kashiwagi T, Harris RH Jr, Zhang X, Briber RM, Cipriano BH, Raghavan SR, et al. Flame retardant mechanism of polyamide 6–clay nanocomposites. Polymer. 2004;45:881–91.

16. Lichtenhan JD, Vu NQ, Carter JA, Gilman JW, Feher FJ. Silsesquioxane-siloxane copolymers from polyhedral silsesquioxanes. Macromolecules. 1993;26(8):2141–2.
17. Haddad TS, Lichtenhan JD. Hybrid organic-inorganic thermoplastics: styryl-based polyhedral oligomeric silsesquioxane polymers. Macromolecules. 1996;29(22):7302–4.
18. Devaux E, Rochery M, Bourbigot S. Polyurethane/clay and polyurethane/POSS nanocomposites as flame retarded coating for polyesters and cotton fabrics. Fire Mater. 2002;26:149–54.
19. Ramirez C, Rico M, Barral L, Diez J, Garcia-Garabal S, Montero B. Organic/inorganic hybrid materials from an epoxy resin cured by an amine silsesquioxane. J Therm Anal Cal. 2007;87:69–72.
20. Dell'Erba IE, Williams RJJ. Epoxy networks modified by multifunctional polyhedral oligomeric silsesquioxanes (POSS) containing amine groups. J Therm Anal Cal. 2008;93:95–100.
21. Villanueva M, Martin-Iglesias JL, Rodriguez-Anon JA, Proupin-Castineiras J. Thermal study of an epoxy system DGEBA ($n = 0$)/MXDA modified with POSS. J Therm Anal Cal. 2009;96:575–82.
22. Fina A, Abbenhuis HCL, Tabuani D, et al. Metal functionalized POSS as fire retardants in polypropylene. Polym Degrad Stab. 2006;91:2275–81.
23. Liu L, Hu Y, Song L, et al. Combustion and thermal properties of OctaTMA-POSS/PS composites. J Mater Sci. 2007;42:4325–33.
24. Jash P, Wilkie CA. Effects of surfactants on the thermal and fire properties of poly (methyl methacrylate)/clay nanocomposites. Polym Degrad Stab. 2005;88:401–6.
25. Duquesne S, Jama C, Le Bras M, Delobel R, Recourt P, Gloaguen JM. Elaboration of EVA-nanoclay systems—characterization, thermal behaviour and fire performance. Compos Sci Technol. 2003;63:1141–8.
26. Samyn F, Bourbigot F, Jama C, Bellayer S, Nazare S, Hull R, et al. Characterisation of the dispersion in polymer flame retarded nanocomposites. Eur Polym J. 1996;32(3):375–83.
27. Liu HZ, Zheng SX, Nie KM. Morphology and thermomechanical properties of organic-inorganic hybrid composites involving epoxy resin and an incompletely condensed polyhedral oligomeric silsesquioxane. Macromolecules. 2005;38:5088–97.
28. Babrauskas V. Specimen heat fluxes for bench-scale heat release rate testing. Fire Mater. 1995;19:243–52.