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Influence of POSS structure on the fire retardant properties of epoxy hybrid networks

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ABSTRACT

Monofunctional Polyhedral Oligomeric Silsesquioxanes (POSS), differing in chemical structure, were introduced into an epoxy-amine formulation in order to obtain hybrid organic/inorganic epoxy networks. The process developed allows the POSS to be either covalently bonded to the network and organized in small amorphous domains, or completely dispersed in larger crystalline domains. Morphology, thermal and fire retardant properties were studied through electron microscopy, DSC, TGA, cone calorimeter experiments and UL94 tests. It was demonstrated that POSS nanoclusters induced an effective fire retardant effect, which was controlled by several factors. It was shown that POSS bearing phenyl ligands were far more effective than POSS with isobutyl ligands, and that the presence of a chemical linkage between the phenyl-based POSS clusters and the matrix favoured the dispersion of the nanoclusters, resulting in enhanced fire retardancy. The fire retardant effect was only slightly enhanced by increasing the amount of POSS nanoclusters.

1. Introduction

Over the last decades the use of polymer materials for a wide range of applications has been considerably and continuously increased, due to certain advantages of plastics over other materials. However, the main drawback that slows further development of polymers is their high flammability. A polymer, as an organic material, will finally end up burning anyway; however scientists, by investigating polymer combustion mechanisms, have developed several techniques for satisfying high levels of fire resistance. By the inclusion of suitable chemicals, termed fire retardants, polymer materials have thus been able to meet high fire safety requirements. Nevertheless, although the majority of flame retardants developed so far have proved to be efficient, several drawbacks are often pointed out: problems during processing of the fire retardant materials, possible reduction in mechanical properties compared to pure polymers, and also the high environmental impact of certain flame retardants such as the brominated additives, widely-used so far, but highly toxic. New directives emanating from the European Union bring dramatic changes to the regulation of the flame retardant market, emphasizing the need to control the storage, handling and disposal of the flame retardants, as well their potential toxicity and smoke emissions during combustion. Particularly the usage of halogenated flame retardants is significantly restricted by several European directives [1]: penta- and octa-bromodiphenylether have been banned by the directive 2003/11/EC since August 2004 and the European member states must ensure since July 2006 that no polybrominated diphenyl ethers are contained in electrical and electronic products marketed in Europe.

The issues concerning the flame retardant market lead scientists to seek new fire retardancy routes for polymer materials, particularly for thermoplastics. A large number of recent papers have focused on halogen-free systems with significant emphasis on phosphorous-based flame retardants but also on nanostructured polymer systems which have shown themselves to be of great interest for flame retardancy [2]. Recent developments in the nanostructure field have helped scientists to better understand the action of this kind of materials, even though the full mechanisms are still not fully understood. Fire retardant nanostructured polymers can be obtained basically via two routes: i) by the use of preformed nanoparticles, the most significant example being layered silicate (montmorillonite) [3–6], but also pyrogenic silica, carbon nanotubes, etc…ii) by the use of organic/inorganic nanoclusters, which are compounds designed on a molecular scale which can hierarchically assemble to form complex structures within the polymer matrix into which they are introduced. Polyhedral Oligomeric SilSesquioxanes (POSS) are the most widely known and

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studied clusters [7–9]. Their architecture is based on a well defined polyhedral cage with general formula $(RSiO_{3/2})_n$, n varying from 6 to 18. Silica and oxygen atoms assemble into an inorganic silica-like core of precise geometry. The inorganic core of POSS is surrounded by organic ligands covalently bound to the Si atoms placed at the vertices of the polyhedral cage. Typical organic ligands are hydrogen, halogen, alkyl groups, organofunctional groups, etc. A general concern about POSS clusters is the high level of interactions existing between clusters, which make some POSS hardly miscible with some monomers or polymers. The nature of the organic ligands of POSS clusters is consequently a crucial element to choose, as it controls the behaviour of the clusters during processing and polymerization, and thus enables chemists to tailor the desired microstructure for the POSS hybrid polymer systems.

The objective of this work was to evaluate the potential of this latter nano-object, i.e. polyhedral oligomeric silsesquioxane, as a fire retardant in epoxy networks as some recent work suggested [10–14]. Epoxy-based thermosetting networks are known to have excellent characteristics such as solvent and chemical resistance, low shrinkage on cure, good adhesion to many substrates, good mechanical properties and outstanding electrical insulating properties [15,16]. However, epoxy networks like most polymers lack thermal and flame resistance, particularly in certain applications where flame retardancy is a required feature. The electronics industry has always been asking for flame retardant epoxy resins in order to meet specific requirements for applications such as integrated circuits, printed wiring boards, semiconductor encapsulation. Additionally, in the transportation field today (automotive, military and commercial aircraft, etc.), epoxy resins are often used as matrices in composite parts and need to have sufficient thermal and flame resistance.

The general idea of this work is on one hand to carefully analyze the different factors that may influence the morphologies generated when POSS nanoclusters are incorporated into epoxy-based networks and on the other hand to understand how the organized nanostructures obtained and the POSS chemical structure may influence the final properties, and particularly fire retardancy. Special attention is given to two defined factors:

- The nature of the inert organic ligands borne by the POSS cages, since it controls the solubility of the POSS-epoxy hybrid systems from the initial reactive mixture to the final crosslinked network. Therefore two types of ligands have been selected, aromatic rings or isobutyl groups; different behaviours were expected considering the chemical structure of the epoxy matrix.
- The presence of possible covalent bonds between the POSS nanoclusters and the epoxy network, since it may affect the polymerization-induced phase separation process and may be responsible for the generation of specific self-assemblies of the nano-objects.

2. Experimental

2.1. Materials

The thermosetting matrix considered in this work was obtained via the polycondensation of an epoxy-amine system. The diepoxy prepolymer used was a DGEBA (diglycidyl ether of bisphenol-A, DER330 from Dow Chemicals); it is liquid at room temperature. Its viscosity is equal to ca. 10 Pa*s at 25 °C. The curing agent used, MDEA (4,4′ methylene bis(2,6-diethylaniline), from Lonza), is a primary aromatic diamine. It has a short and rigid chain so that the network obtained in combination with DGEBA DER330 shows a high crosslink density, and is glassy at room temperature [17].

Three types of POSS nanoclusters have been selected for this research. They contain two types of non reactive ligands: isobutyl or phenyl. Isobutyl groups generate weaker POSS–POSS interactions than phenyl groups as verified by the lower melting point, which facilitates their reaction with the amine. Two of the POSS have a glycidyl functional group which can react with the amino groups from the curing agent MDEA; the third POSS has no reactive group. All the POSS™ products were purchased from Hybrid Plastics co. (Hattiesburg, MS, USA).

The chemical structure of all the chemicals used here and their associated abbreviations used are shown in Table 1. They were used as received.

2.2. Processing

2.2.1. Neat epoxy matrix

The desired amounts of amine and epoxy monomers (amino hydrogen/epoxy cycle = $a/e = 1/1$) were mixed together, under vacuum, at 90 °C using mechanical stirring in order to melt the MDEA and get an homogeneous mixture. The crosslinking was carried out according to the following cure schedule: 4 h at 135 °C, followed by a post-cure for 4 h at 190 °C. The glass transition temperature of this network is equal to 173 °C as measured by DSC (heating rate = 10 °C/min).

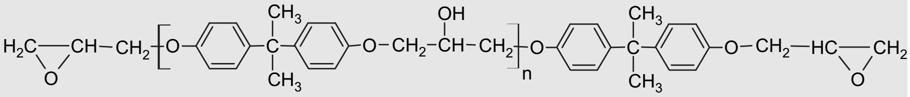
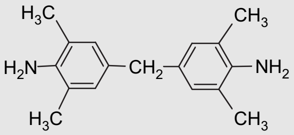
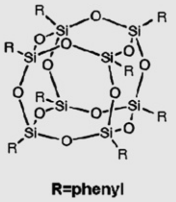
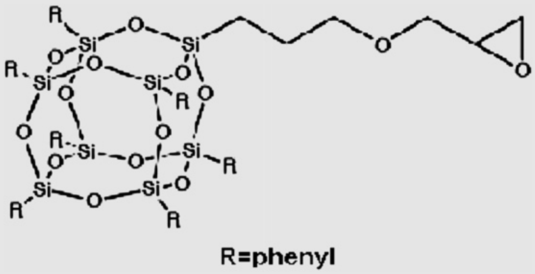
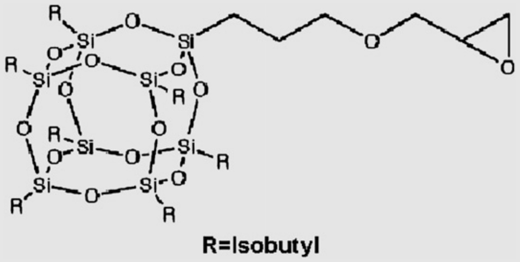
2.2.2. Synthesis of epoxy hybrid networks containing monofunctional POSS clusters

In order to ensure the chemical reaction between the reactive POSS clusters and the epoxy matrix, a two-step synthesis was carried out for this type of nanocluster [18]. In a first step, the pre-reaction of the monofunctional POSS nano-objects with MDEA was performed through the classical epoxy–amine reaction. The required amount of POSS was reacted in excess of amine at high temperature and for sufficiently long time, as determined by size exclusion chromatography, to ensure total reaction of the POSS clusters. Table 2 gives the amounts of POSS:MDEA used. For Gly-iBu POSS, the mixture with MDEA was homogeneous and the reaction was carried out at 150 °C during 10 h to ensure full reaction of Gly-iBu POSS with MDEA. By contrast, the Gly-Ph POSS nano-objects were not soluble into the amine co-monomer and could not be melted either. Previous dissolution of Gly-Ph POSS and MDEA in THF was thus carried out, followed by solvent evaporation, in order to ensure fine dispersion of the POSS aggregates. The pre-reaction with Gly-Ph POSS therefore took place in a heterogeneous medium, with the POSS still being crystalline in the initial blend. The reaction was carried out at 150 °C for 5 h, followed by 1 h at 200 °C and 1 h at 220 °C. It was necessary to increase the temperature to ensure a maximum reaction of Gly-Ph POSS with MDEA. In a second step, the epoxy networks were synthesized by adding the corresponding amount of DGEBA. Mechanical stirring at 90 °C for 15 min was carried out, followed by cure and post-cure. The materials obtained were transparent. The hybrid networks processed using the two-step synthesis were denoted pre-reacted POSS networks.

2.2.3. Synthesis of epoxy hybrid networks containing nonfunctional POSS clusters

Octaphenyl POSS clusters were mixed with the required amount of amine in tetrahydrofuran (THF) in order to favour the dissolution and dispersion of the clusters within the monomers. Nevertheless, OctaPh POSS is poorly dissolved in THF and the solution remained cloudy. After THF evaporation, the stoichiometric amount of DGEBA was introduced and the mixture mechanically stirred at 90 °C for 15 min. The mixture was still heterogeneous, as the final material resulted opaque.

Table 1
Components used.

Name	Denomination	Schematic structure
Diglycidyl ether of Bisphenol-A	DGEBA	
4,4′-methylenebis(2,6-diethylaniline)	MDEA	
Octaphenyl-POSS™ (Ref. MS0840)	OctaPh POSS	
glycidyloxypropyl-heptaphenyl-POSS™ (Ref. EP0425)	Gly-Ph POSS	
Glycidyloxypropyl-heptaisobutyl-POSS™ (Ref. EP0418)	Gly-iBu POSS	

In general, POSS were loaded at two weight fractions, corresponding to 1.5 and 3.7% inorganic content. All networks were crosslinked using the same curing cycle which ensure complete reaction of epoxy with amino groups.

Table 2
Composition of POSS-based epoxy networks.

Type of POSS used	POSS content			MDEA	DGEBA
	Inorganic part [wt%]	[wt%]	[mol]	[mol]	[mol]
OctaPh POSS	1.50	3.73	1	26.9	53.7
	3.70	9.19	1	10.9	21.8
Gly-Ph POSS	1.50	3.86	1	26	51.5
	3.71	9.55	1	10	19.5
Gly-iBu POSS	1.51	3.38	1	16	51.5
	3.75	8.41	1	10	19.5

2.3. *Techniques*

2.3.1. *Morphology*

Scanning Electron Microscopy (SEM) examination was performed using a Jeol JSM 6400 microscope on fracture surfaces coated with a gold layer.

2.3.2. *WAXS*

Wide Angle X-Ray Scattering (WAXS) experiments were performed on a Siemens D500 X-ray diffractometer, operated at 40 mV and 30 mA and CuKα radiation.

2.3.3. *Differential scanning calorimetry*

DSC was carried out using a DSC30 Mettler Toledo under inert atmosphere using a scan rate of 10 K/min and over a temperature range of 25–250 °C.

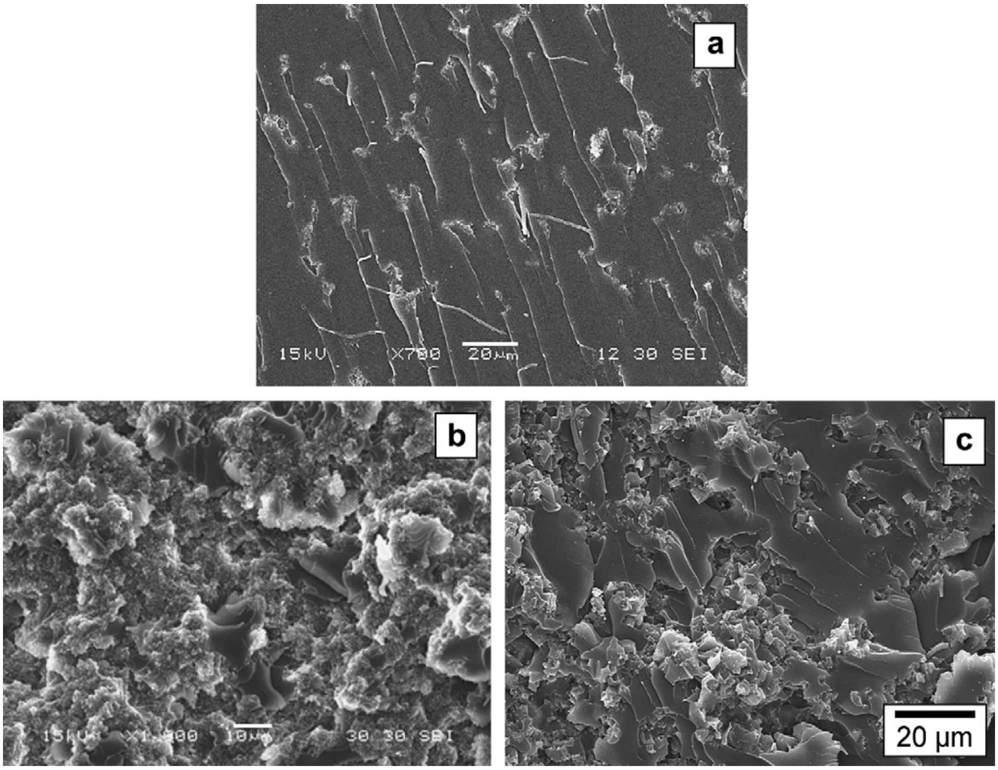


Fig. 1. SEM micrographs of final morphologies generated in DGEBA–MDEA epoxy networks modified with POSS (3.7 inorganic wt%): (a) pre-reacted Gly-iBu POSS. (b) pre-reacted Gly-Ph POSS (c) non reactive OctaPh POSS.

2.3.4. Thermogravimetric analysis

TGA analyses were carried out in air or under inert atmosphere (10 K min^{-1}) using a TGAQ500 from TA instruments. The specimens (weight 10 mg) were placed in a platinum holder.

2.3.5. Combustion tests

These were performed on a Fire Testing Technology Cone Calorimeter, with 50 × 50 × 6 mm specimens; the external heat flux was equal to 35 kW/m^2. Such a value is closed to the conditions of a mild fire scenario [19]. Specimens were wrapped in an aluminium foil leaving the upper surface exposed to the radiator. Three tests were performed for each sample and in following sections the average values will be discussed. UL94 tests were also performed on the different POSS-based epoxy networks. Samples of 120 × 10 × 2 mm size were held vertically and ignited by a standard Bunsen burner. Two sets of five parallel specimens were tested. Flame classification used was ASTM D3801.

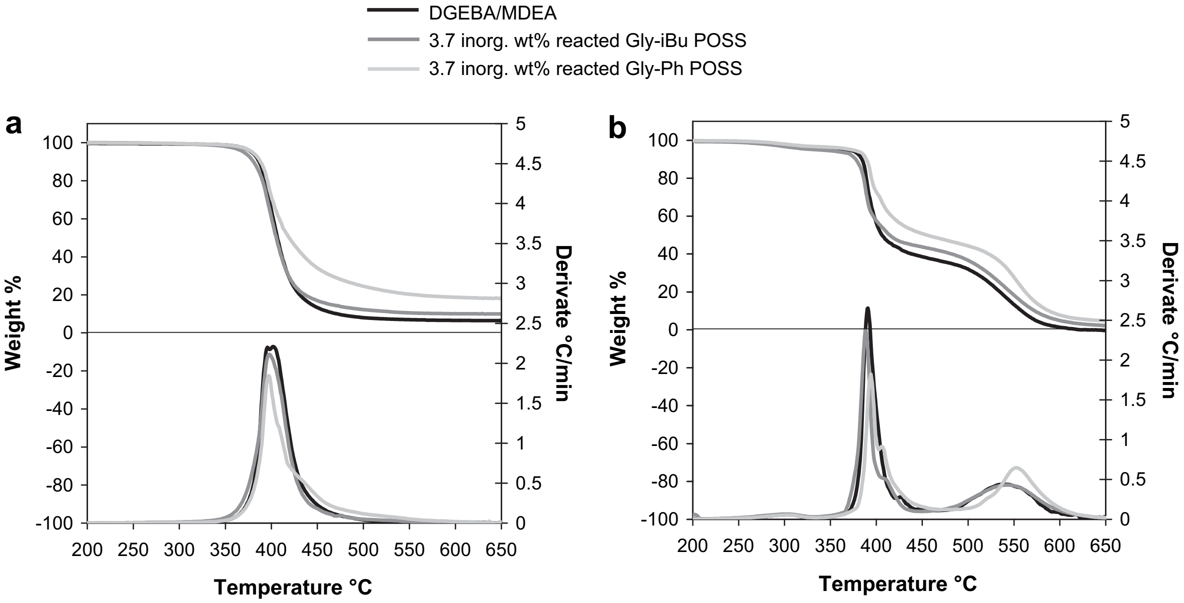


Fig. 2. TGA curves of epoxy networks containing 3.7 inorg. wt% of pre-reacted Gly-iBu POSS and Gly-Ph POSS in inert atmosphere (a) and in air (b) (10 K min^{-1}).

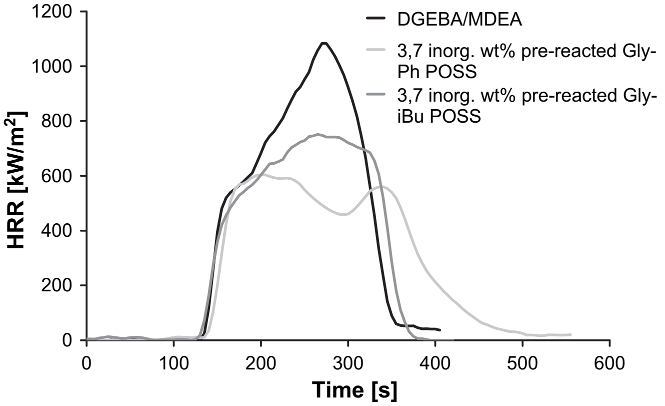


Fig. 3. Heat release rate (HRR) as a function of time for epoxy networks containing 3.7 inorg. wt% of pre-reacted Gly-iBu POSS and pre-reacted Gly-Ph POSS: Effect of POSS non reactive ligands.

3. Results and discussion

The thermal stability and fire retardant properties of the POSS hybrid epoxy networks were examined using both TGA, cone calorimeter analyses and UL94 test and investigated as a function of the different parameters that may to influence the resulting morphologies of the POSS-epoxy networks, *i.e.* the nature of non-reactive ligands, the presence of pre-reaction, and the POSS weight fraction.

3.1. *Influence of the non-reactive groups: phenyl vs. isobutyl on morphology and fire retardancy*

In a previous work [18,20], the study of reaction kinetics and polymerization in the POSS/DGEBA/MDEA system revealed that polymerization-induced phase separation took place with monofunctional POSS clusters (either Gly-iBu POSS or Gly-Ph POSS) even when they were pre-reacted with the curing agent MDEA. Fig. 1a and b show SEM micrographs obtained on the DGEBA-MDEA epoxy networks modified with Gly-iBu POSS and Gly-Ph POSS respectively, pre-reacted with MDEA in a first step as described in Experimental section. Different network morphologies were obtained: in the first case, phase separation led to the formation of irregular POSS aggregates composed by a set of small individual domains; in the second case, a more complex morphology could be identified composed by a smooth phase, assigned to the epoxy-amine matrix, and a rough phase (largest area), thought to be the POSS-rich phase.

In the present study, the glass transition temperature of the processed networks was determined by DSC and it was observed that the difference in POSS structure and miscibility has an impact on the value of the Tg. The glass transition temperature of the system containing 3.7 inorg. wt% of Gly-Ph POSS is $T_g = 171$ °C, which is close to the value of the neat matrix (equal to 173°). When isobutyl ligands surround the POSS cages, a higher decrease is observed: Tg is found equal to 156 °C. Since both POSS clusters are effectively linked to the matrix, the difference may be explained by the more rigid structure of the Gly-Ph POSS clusters and the presence of aromatic rings in its structure, the Gly-Ph POSS acting as an anchoring point, lowering the mobility of the network. Isobutyl groups, by contrast, may induce more flexibility and are more likely to move around.

Therefore, it can be concluded that the nature of the organic ligands borne by the POSS cages, *i.e.* phenyl vs. isobutyl groups, has a significant influence on the morphologies generated and glass transition reached. The better compatibility of the phenyl ligands with the epoxy-amine components compared with the isobutyl ligands, leads to completely different morphologies.

Thermal and oxidative degradation of the neat matrix and the networks containing 3.7 inorg. wt% of pre-reacted POSS nanoclusters bearing different non reactive ligands are illustrated in the TGA curves reported on Fig. 2.

In nitrogen, pure epoxy resin thermally degrades through a single step process with maximum rate at 403 °C leaving a residue during which extensive break down of chemical bonds of the epoxy network takes place including C-phenyl bonds of bisphenol-A, leading to almost complete volatilization (Fig. 2a). A minor amount of charred residue is formed (ca. 6.5 wt%) due to limited recombination to a thermally stable charred material of reactive degrading species during decomposition [21].

Once again, differences are observed in the thermal decomposition of the hybrid networks. In inert atmosphere, whereas the POSS clusters containing isobutyl ligands do not significantly affect the degradation pathways of the epoxy networks, POSS clusters containing phenyl ligands modify the decomposition process. Modifications in the decomposition mechanisms are found to take place above 400 °C, leading to an overall slower degradation and to the formation of strong char residue (residue content of 18.2 compared to 9.9 wt% for isobutyl-based POSS at the end of the decomposition). The thermal behaviour of pure POSS was shown to depend on substituent type [22]: iBu POSS showed evaporation in inert atmosphere with a maximum weight loss, $T_{\max}$, equal to 272 °C, while Ph POSS showed a higher thermal stability (up to 350 °C), did not undergo volatilization and produces a considerably higher residue with respect to iBu POSS. The differences observed are due to the intrinsic stability of the organic group. Therefore the tendency of Gly-Ph POSS nanoclusters to char in inert atmosphere compared to Gly-iBu POSS, makes this system more active in protecting the epoxy matrix from thermal degradation, thus promoting the formation of a stable residue, although not substantially modifying its degradation.

The epoxy network shows good resistance to thermal oxidation since the weight loss curves of neat epoxy in nitrogen and air are coincident up to 400 °C. However, charring of the epoxy network takes place in air at a higher yield (ca. 44% at 420 °C) due to catalysis by oxygen [21]. Complete oxidation-combustion of the char takes place in air with maximum rate at 540 °C (Fig. 2b).

In air a trend similar to that reported in nitrogen could be observed: when phenyl-based POSS clusters are introduced, a strong enhancement in the weight retention is observed soon after the beginning of the degradation (around 400 °C). Reasons for this behaviour are to be found in the same mechanism proposed for the degradation in nitrogen, due to the higher tendency of pristine Gly-Ph POSS to form a ceramic residue, thus protecting epoxy from degradation and favouring char formation. Indeed at the end of the first degradation step (ca. 420 °C) pure epoxy produces a 44% residue while the presence of Gly-Ph POSS increases this value up to 58%. Additionally, the complete char degradation, which for pristine epoxy and Gly-iBu POSS containing network has a maximum weight loss rate at 540 °C, is delayed in the case of Gly-Ph POSS of about 20–30 °C.

Table 3
Comparison of time to ignition and HRR max of epoxy networks (average values over 3 samples for hybrid networks, over 6 values for neat epoxy network).

Material	T_{ignition} (s)	$HRR_{\max}$ (KW/m^2)	Improvement (%)
Neat epoxy	132 ± 16	1040 ± 74	/
+ 3.7 wt% pre-reacted Gly-Ph POSS	153 ± 6	622 ± 20	40
+ 3.7 wt% pre-reacted Gly-iBu POSS	129 ± 12	782 ± 25	25
+ 3.7 wt% OctaPh POSS	140 ± 17	689 ± 43	34

Fig. 4. Cross sections of cone calorimeter residues of POSS-epoxy hybrid systems: (a) neat epoxy matrix, (b) 3.7 inorg. wt% pre-reacted Gly-Ph POSS, (c) 3.7 inorg. wt% OctaPh POSS.

It has been shown that Gly-iBu POSS clusters as well form a thermally stable residue when decomposed in air, but it seems that no effect is exhibited in the resulting POSS-epoxy networks. The residues after decomposition in air correspond approximately for both systems to the amount of the inorganic part of the POSS nanoclusters introduced.

It is therefore straightforward that the chemical nature of the POSS clusters is able to strongly affect epoxy degradation.

The differences observed for the systems containing POSS nanoclusters with different non reactive ligands are also well reflected in the flame retardant behaviour, as shown in the Heat Release Rate, HRR, curves reported in Fig. 3 and in the values to time of ignition and peak of HRR reported in Table 3. The fire behaviour is clearly modified by the presence of the POSS clusters: for both types of POSS cages, a significant decrease is observed in the peak of heat release rate which is a major parameter in controlling flame propagation of fire. In the case of POSS with phenyl groups, a higher decrease of HRR peak is noticed: the peak of HRR is decreased by 40% in this case as compared to 25% for isobutyl-based POSS network. The time to ignition is also slightly increased. Moreover, the burning process seems to proceed for Gly-Ph POSS based hybrid in two separate phases, probably because of the formation of a protective structure in the early stages of the burning phase, which is degraded after 300 s from ignition thus providing new fuel to the flame and accounting for an increased heat released before flaming out.

Some interesting information is provided by visual observation of the end of test residues (Fig. 4). On cross sections of the residues it can be seen that the Gly-Ph POSS nanoclusters form during combustion a solid sponge-like structure (Fig. 4b) that is not formed on neat epoxy network (Fig. 4a) or in presence of isobutyl-containing POSS clusters. Remarkable reduction of HRR values observed for Gly-Ph POSS hybrid networks is likely to be due to the presence of this char layer formed during combustion. The char layer generated is thought to act as a barrier for both heat flow and mass transport, as observed in other POSS-containing polymer materials [9,23,24].

UL94 vertical burning tests have also been carried out on these POSS-epoxy hybrid systems and the results are consistent with the cone calorimeter results. Neat epoxy network and the network containing POSS bearing isobutyl ligands exhibit the worst results

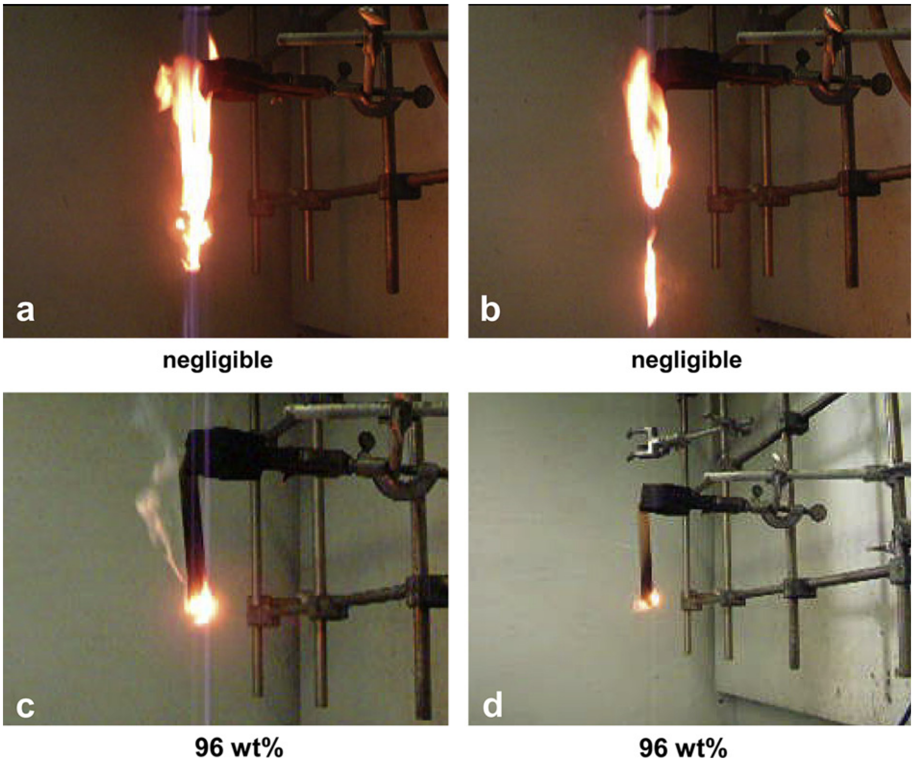


Fig. 5. UL-94 vertical test pictures and the corresponding residual weight: (a) neat epoxy matrix, (b) 3.7 inorg. wt% pre-reacted Gly-iBu POSS, (c) 3.7 inorg. wt% pre-reacted Gly-Ph POSS and (d) 3.7 inorg. wt% non reactive OctaPh POSS.

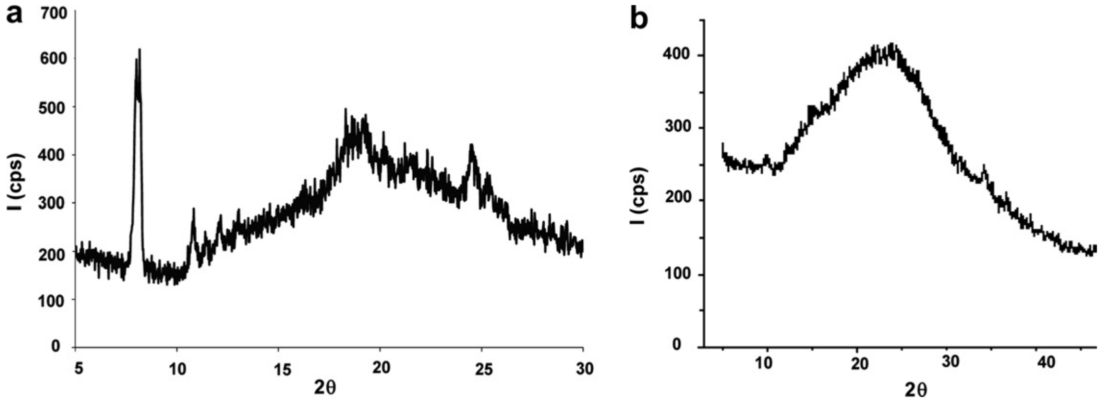


Fig. 6. X-ray diffraction spectra of : (a) epoxy network modified with 3.7 inorg. wt% OctaPh POSS and (b) epoxy network modified with 3.7 inorg. wt% pre-reacted Gly-Ph POSS.

in terms of fire retardancy performances: all these materials burned until clamps with release of incandescent drops (Fig. 5a and b). On the other hand, epoxy network containing Gly-Ph POSS (Fig. 5c), although not classified under ASTM D3801 standard, show better results in UL94 tests with self extinguish flames. In addition, no release of drops is observed and the weight of the end of test residue is in this case 96 wt%, this confirming the tendency to phenyl-containing POSS to promote charring during epoxy combustion.

3.2. *Effect of a pre-reaction*

Comparison between epoxy networks containing effectively-bonded Gly-Ph POSS clusters and non reactive OctaPh POSS has been made. OctaPh POSS nanoclusters are initially poorly soluble in the reactive epoxy-amine precursors.

The glass transition temperatures, measured by DSC, of both systems are similar (171 °C). In the case of the non reactive POSS, it is not expected a strong influence on Tg, since the POSS nanoclusters are not part of the network. By contrast, the morphologies are slightly different (Fig 1b and c). In both systems, two different phases are observed: a smooth phase that has been assigned to the epoxy-amine matrix and a rough phase corresponding to the POSS-rich phase, but with different proportion of each phase. The network containing non reactive OctaPh POSS exhibits large area of smooth phases while the surface of the network modified with the pre-reacted Gly-Ph POSS is almost completely rough, suggesting that a much more homogeneous dispersion of the nanoclusters is achieved in the later case. The phenyl ligands borne by the POSS nano-objects favour the dispersion of the nano-objects within the matrix, owing to affinity in the chemical structure of the different components and thus an extensive interaction between POSS and matrix can be developed. It is suggested that, when the POSS are pre-reacted, they act as a kind of surfactant where the POSS/epoxy balance facilitates the homogeneous distribution of the POSS-rich domains within the matrix.

The possibility that POSS could form crystalline domains was investigated using X-Ray diffraction. XRD spectra of pure Gly-Ph POSS, OctaPh POSS and of the networks modified by non reactive OctaPh POSS and pre-reacted Gly-Ph POSS have been recorded [20]; XRD spectra for the two networks are shown in Fig. 6. The sharp peak present at 8° in Fig. 6a constitutes a clear indication that OctaPh POSS form crystalline domains; but the amorphous halo evidenced in Fig. 6b is the proof that the dispersed clusters from pre-reacted Gly-ph POSS are amorphous. POSS crystals are present when no covalent bond exists between the clusters, i.e. OctaPh POSS, and the matrix, but disappear when a pre-reaction is carried out, accounting for a more homogeneous distribution of POSS molecules inside the epoxy network, which prevents their aggregation in large crystals detectable by XRD analysis.

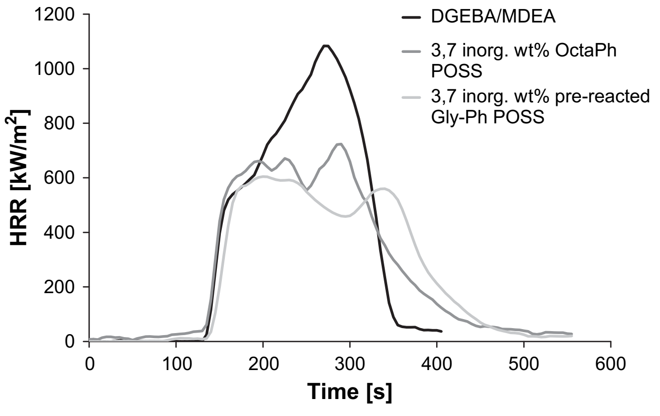


Fig. 7. Heat release rate (HRR) as a function of time for epoxy networks containing 3.7 inorg. wt% of non reactive OctaPh POSS and pre-reacted Gly-Ph POSS.

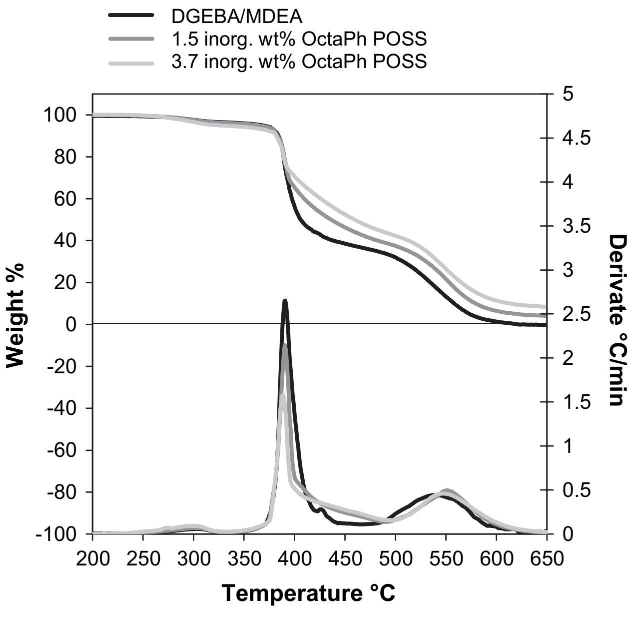


Fig. 8. TGA curves of epoxy networks containing different amounts of non reactive OctaPh POSS in air – effect of POSS content.

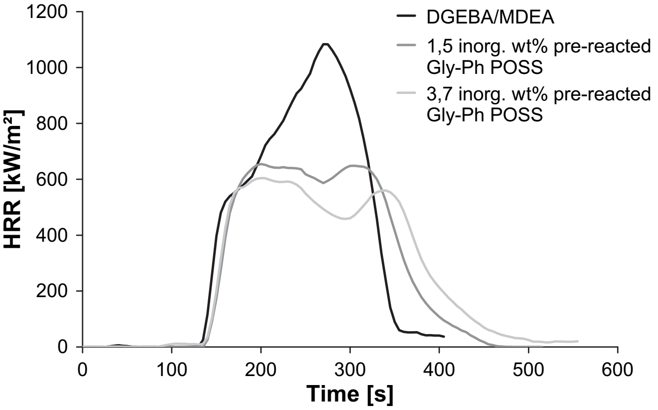


Fig. 9. Heat release rate (HRR) as a function of time for epoxy networks containing different amount of pre-reacted Gly-Ph POSS: Effect of POSS content.

Fig. 7 gives the heat release rates as a function of time for epoxy networks containing 3.7 inorg. wt% of non reactive OctaPh POSS and pre-reacted Gly-Ph POSS. As it can be seen in the data reported in Table 3, a remarkable reduction in the HRR peak is exhibited for both POSS-epoxy networks, with a decrease equal to 34% and 40% for OctaPh POSS and Gly-Ph POSS clusters, respectively, as compared to the neat network and with a very similar two-step process.

Both POSS nanoclusters cause the charring of the material during combustion, which may reasonably explain the decrease of HRR peak observed. However, the structures formed differ, depending on the type of POSS used (Fig. 4). Non reactive OctaPh POSS nanoclusters bring about the formation of a rigid but brittle thin layer on the top of the burning material whereas pre-reacted GlyPh POSS cause the formation of a rigid sponge-like structure that is not only on the top of the samples (Figs. 4c andb respectively). This difference in the char structure may account for the difference observed in the reduction of the HRR peak. The better performances observed with Gly-Ph POSS clusters may result from the better dispersion of the POSS nanoclusters when covalent bonds exist between POSS and matrix, impeding repelling of the POSS to the surface, and therefore permitting charring of the whole samples.

Both OctaPh- POSS and GlyPh- POSS hybrid epoxy networks (Figs. 5d andc) exhibited self extinguish flames, with no release of drops and weights at the end of the test comparable (96 wt%).

The present study shows that the morphology and the degree of crystallinity of POSS-epoxy hybrid networks are determined by both the nature of the non-reactive groups and the presence or not of a pre-reaction which allows the linking of the POSS clusters to the network by covalent bond. However, the fire retardancy performances of the corresponding networks appear to be more influenced by the nature of the non-reactive ligands borne by the POSS cages, rather than the presence of a chemical linkage between POSS and matrix, although this late parameter leads to a completely distinct morphology. In the case of POSS containing phenyl-groups, the decrease in the peak of HRR observed has been ascribed to the initial tendency of the phenyl-containing POSS to char when decomposing.

3.3. *Effect of POSS weight fraction*

The effect of the POSS weight fraction has been investigated for both isobutyl and phenyl-based clusters.

In the case of phenyl-based POSS clusters, differences are observed in the thermal degradation of the corresponding networks. Fig. 8 gives the TGA curves obtained for systems containing different amounts of OctaPh POSS. The same types of curves are observed for the pre-reacted GlyPh POSS (not shown here). It is observed that an increasing enhancement in the weight retention is observed after the beginning of the degradation with increasing POSS content.

As far as combustion is concerned, we can underline that the performances depicted for 3.7 wt% loading can also be reached with 1.5 wt% loading, further addition of POSS not bringing significant improvements (Fig. 9). This confirms that, when the chemical nature of the POSS is favourable, these systems can strongly influence the fire behaviour even at very low concentrations.

On the other hand, the weight of the end of test residues after UL 94 tests is function of the POSS content, with values of 70 and 96 wt% for the epoxy networks containing 1.5 and 3.7 inorg. wt%, respectively.

Fig. 10 illustrates the HRR curves obtained for epoxy networks containing different amounts of non-reactive OctaPh POSS and pre-reacted Gly-iBu POSS clusters. Slight differences are noticed but compared to the other factors that influence the fire retardant behaviour, it is clear that the amount of POSS clusters affects the fire retardancy to a lesser extent.

4. Conclusions

Different types of polyhedral oligomeric silsesquioxane have been introduced into an epoxy system in order to prepare hybrid

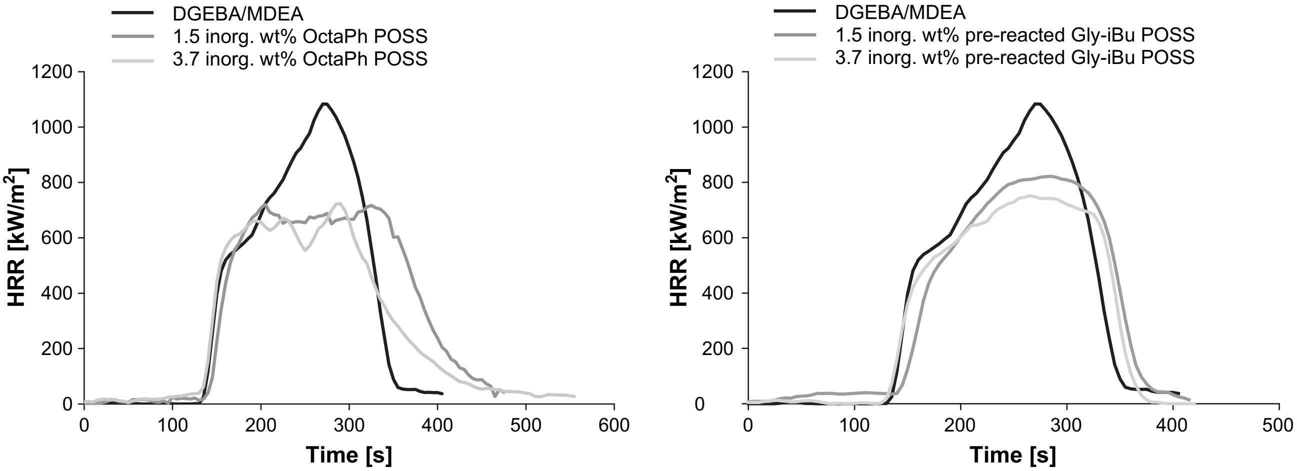


Fig. 10. Heat release rate as a function of time for epoxy networks containing different amount of non reactive OctaPh POSS and pre-reacted Gly-iBu POSS.

organic/inorganic networks with the objective to see if POSS can be used as a fire retardant additive.

The organization of POSS metal oxo-clusters into the network mainly depends on the nature of the organic ligands borne by the POSS cages, isobutyl groups are less compatible with the aromatic monomers used (DGEBA and MDEA) than are phenyl groups, and on the possible reaction of one of the ligands with the epoxy network. As a function of these key factors, different morphologies and crystalline assemblies of the POSS nanoclusters within the epoxy networks are observed.

Interesting fire retardant properties are reported for certain systems studied. More than the resulting dispersion state/organization of the POSS nanoclusters within the matrix, the nature of the non-reactive ligands borne by the POSS cages significantly influences the flammability of the resulting hybrid network. POSS nanoclusters bearing phenyl groups lead to a drastic reduction of the peak of heat release rate. This effect has been attributed to formation of a char layer induced by the presence of the POSS clusters in epoxy matrices. The use of pre-reacted monofunctional phenyl-based POSS, in contrast with the non-reactive phenyl POSS, leads to a better and more homogeneous dispersion of the nanoclusters within the matrix, because they are all covalently bonded to the network, and it favours the formation of a rigid sponge-like structure after combustion. The presence of this char is thought to act as barrier for both heat flow and mass transport and impeding the release of incandescent drops in the UL94 test. The formation of the rigid char structure during combustion may be accounted for by the initial tendency of the phenyl-based nanoclusters to char during combustion, particularly in absence of oxygen. The POSS nanoclusters may possibly influence the kinetics of degradation of the epoxy, rather than the mechanisms of degradation, since total heat evolved in the cone calorimeter experiment and the TGA profiles are hardly influenced by the amount of POSS clusters added to the epoxy network.

In summary the use of POSS nanoclusters is a promising route for improved fire retardancy of epoxy materials which involves formation of a rigid char structure during combustion. The non-reactive ligands of the POSS cages have to be carefully selected and the POSS clusters homogeneously dispersed in the network (by using pre-reaction for instance).

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