

## FIRE-RETARDANT EPOXY MATRICES DESIGNED FOR COMPOSITE MATERIALS PROCESSED BY INFUSION

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The epoxy/amine networks were synthesized either from tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) and 4,4'-Methylenebis(2,6-diethylaniline) (MDEA), or from a commercial infusion-suitable formulation. They contained 4wt% of trisilanolPhenyl POSS as a fire retardant, with or without an aluminium catalyst. Morphologies (TEM), thermal stability (TGA) and fire behaviour (UL-94, cone calorimeter) of the networks were assessed. While the morphologies, although intricate, did not differ much between the POSS-containing formulations, the systems containing both POSSOH and the aluminium catalyst showed particularly large fire retardance improvements as compared to the neat matrices and the networks containing POSSOH only.

### 1. Introduction

Thermosetting epoxy polymers are suitable for a wide range of applications but they suffer from a high flammability that is detrimental in terms of human safety, material damage, and psychological impact on public.

Solutions to overcome this main drawback have been found that include introducing halogenated fire retardant compounds in a conventional epoxy polymer, or changing the chemical structure of the epoxy prepolymer (e.g. brominated epoxy resins). Such compounds tend nowadays to be subjected to drastic regulations due to the evolution of European directives such as REACH [1]. Researchers have been looking for alternatives, among which the phosphorus-based compounds, phosphorus-modified resin backbones and/or hardeners have attracted great interest [2-5]. In many cases though, those compounds are to be used in high proportions, which can sometimes bring detrimental changes in other material properties [6]. More recently, inorganic flame retardants, such as silicate clays or carbon nanotubes, have been investigated and a great emphasis has been put on their nanostructuration and its influence on the thermal stability and fire retardancy of the organic/inorganic synthesized networks [7-9].

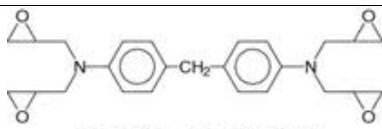
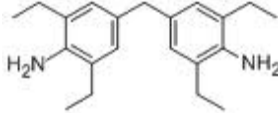
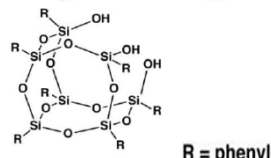
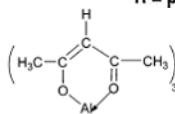
In the last decade, incorporation of Polyhedral Oligomeric Silsesquioxanes (POSS) in epoxy materials has been studied with the target to enhance their fire retardancy. POSS are organic/inorganic materials made of a silica core surrounded by organic ligands. In particular, the POSS-T<sub>8</sub> is a type of POSS with a cubic-shaped cage and of general formula (RSiO<sub>1/2</sub>)<sub>8</sub>,

where R are organic ligands on the silicon atoms. In particular, phenyl-bearing POSS have been found to have a beneficial effect on fire retardancy of epoxy networks over other types of ligands [10]. POSS can be incorporated as non-reactive nano-objects or they can be grafted to the polymer backbone as pendant units or inserted to the polymer chains or network as crosslinking points, depending on their functionality. A particular case of functional POSS is the silanol-containing POSS. The silanol functions were reported to react with the hydroxyl and the oxirane ring of the epoxy prepolymer under the action of metal catalysts [11, 12, 13].

## 2. Experimental

### 2.1. Materials

The study focused on two different epoxy systems designed for structural composite materials used in aeronautics – i.e. with high thermo-mechanical properties. A model system was based on Tetraglycidyl(diaminodiphenyl)methane (TGDDM) as an epoxy prepolymer, and 4,4' methylene bis(2,6-diethylaniline) (MDEA) as a curing agent. The TGDDM (MY9512 from Huntsman) was an aromatic tetrafunctional epoxy prepolymer with an epoxy equivalent weight between 117 and 134 g/eq. The resin was a viscous liquid at room temperature. The MDEA (Lonza), a low reactive, primary aromatic diamine, was a crystalline powder at room temperature. A second system was based on a commercial aeronautic formulation specially designed for the infusion process, the MVR444. It was supplied by Cytek, UK, as a two-component. TrisilanolPhenyl POSS (POSSOH) was purchased from Hybrid Plastics. It was a crystalline powder ( $T_m = 219\text{ }^\circ\text{C}$ ) at room temperature. Aluminium tri(acetylacetonate) (Al catalyst) was purchased from Sigma-Aldrich. All products were used as received. The structures of the model materials and the additives, as well as the abbreviations used for simplification concerns, are reported in Table 2.1.

| Product                                    | Denomination | Functionality | Structure   |
|--|--------------|---------------|---|
| Tetraglycidyl<br>(diaminodiphenyl)methane  | TGDDM        | 4             |   |
| 4,4' methylene bis<br>(2,6-diethylaniline) | MDEA         | 4             |  |
| TrisilanolPhenyl POSS                      | POSSOH       | 3             |  |
| Aluminium acetylacetonate                  | Al           |               |  |

**Table 1.** Chemical structure of model materials and additives

### 2.2. Processing

Neat epoxy networks were produced as reference systems. For both systems, the epoxy prepolymer and the hardener were mixed in a stoichiometric amount under vacuum and

mechanical stirring at 90°C for about 20 minutes – until obtaining a homogeneous solution. The mixture, called TM or MVR, was then cast into closed moulds (dimensions: 150 x 150 x 4.2 mm for UL94 tests and 235 x 130 x 4.2 mm for cone calorimeter samples) and cured in oven according to the curing cycle given in Table 2.2.

For the hybrid thermoset network production, the desired amount of POSSOH was dispersed in either the TGDDM or the MVR444 epoxy prepolymer at 130°C ( $\pm 5^\circ\text{C}$ ) for at least 30 minutes, under vacuum and mechanical stirring. The mixture was then slowly cooled to 90°C before addition of a stoichiometric amount of MDEA or MVR444 hardener, respectively, and further stirred for 30 minutes until obtaining an homogeneous solution. In Al-containing networks, addition of the catalyst was carried on at this stage and the mixture was stirred at 90°C for 5 minutes until complete dissolution of the catalyst. The mixtures were then cast in closed moulds and cured in oven. Compositions, curing cycles and final glass transition temperature of all systems are detailed in Table 2. The first dwell temperature was lowered in the curing cycle of Al catalyst-containing networks as it was shown that the combination of POSSOH and Al catalyst shortened the gelation time at 135°C (results not presented in here).

| Networks       | POSSOH (wt%) | Al catalyst (wt%) | Curing cycles                          | Tg (°C) |
|----------------|--------------|-------------------|--|---------|
| TM             | -            | -                 | 4h at 135°C / 3h at 200°C              | 216     |
| TM-POSSOH-130  | 4.1          | -                 |  | 214     |
| TM-POSSOH-Al   | 4.1          | 0.4               | 2h at 90°C / 2h at 135°C / 3h at 200°C | 206     |
| MVR            | -            | -                 | 4h at 130°C / 2h at 180°C              | 216     |
| MVR-POSSOH-130 | 4.1          | -                 |  | 215     |
| MVR-POSSOH-Al  | 4.1          | 0.4               | 2h at 90°C / 2h at 130°C / 2h at 180°C | 211     |

**Table 2.** Compositions and curing cycles of epoxy networks. Tg of the networks were assessed via DSC (10 K.min<sup>-1</sup> from 25 to 250°C under inert atmosphere).

### 2.3. Characterization methods

TEM observations were carried out using a Philips CM120 at an acceleration voltage of 80kV. The samples were trimmed using a ultramicrotome machine at room temperature.

TGA analyses were performed with a TGAQ500 from TA Instruments, under air and inert atmosphere. The temperature range was of 20 to 800°C, the ramp rate of 10 K.min<sup>-1</sup>. The specimens were placed in a platinum holder.

The UL-94 test was performed according to the standard ASTM D3801. The rectangular samples (13 x 125 x 4.2 mm<sup>3</sup>) were cut out of bigger plates and their edges polished. Five to six specimens were tested for each system.

The cone calorimeter experiments were performed with a Fire Testing Technology equipment, according to standard ISO 5660. Square samples of 100 x 100 x 4.2 mm were cut out of bigger manufactured plates and their edges were polished. They were wrapped in an aluminium foil on their lower surface and placed on an insulated sample holder. The sample holder was left to cool to room temperature between each test. The heat flow implemented during the test was of 50 kW.m<sup>-2</sup> and the samples were ignited with a spark. Four specimens were tested for each system.

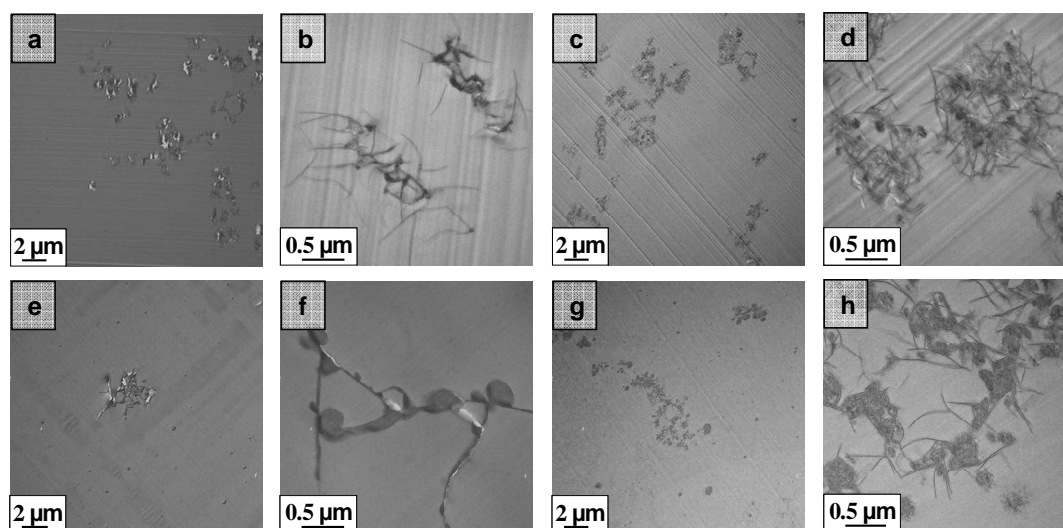
### 3. Results

#### 3.1. Morphology

Dispersion of the POSS nano-objects, i.e. morphologies of organic/inorganic hybrid polymer networks is a key parameter for tailoring the final properties of the networks. The POSSOH being solubilised prior to curing, the final morphology is then controlled by the possible interactions the POSS is likely to create within the network and the phase separation arising during the curing process.

The network morphology was investigated using Transmission Electron Microscopy (Figure 1). The dark zones were attributed to POSSOH, as silicon has a higher atomic weight than the hydrocarbon epoxy matrix. POSSOH molecules arranged themselves in the form of threads or filaments, forming non-continuous inorganic network-like domains.

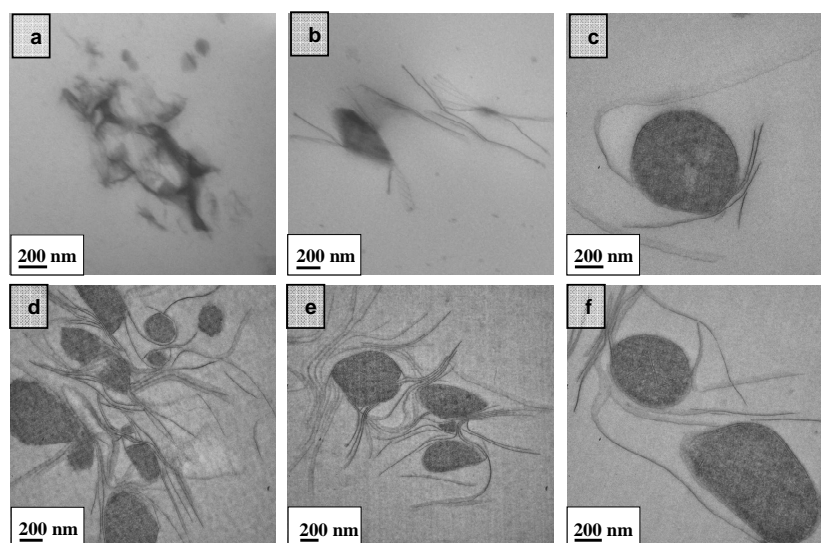
In the case of the aluminium catalyst-containing networks, the POSSOH domains were smaller and denser as compared to the non-catalysed systems. The filaments were well defined, and some nodules around 0.1-0.2  $\mu\text{m}$  were present within the ‘filament network’. Nodules were also observed in the MVR-POSSOH-130 network within the matrix. In TM-POSSOH-130 and MVR-POSSOH-130 networks, these domains were larger and the POSSOH seemed less well arranged, with fewer filaments around diffuse nucleus of POSSOH and epoxy.



**Figure 1.** TEM micrographs of a, b) TM-POSSOH-130; c, d) TM-POSSOH-Al; e, f) MVR-POSSOH-130; g, h) MVR-POSSOH-Al. Pictures b, d, f and h are higher magnifications of pictures a, c, e and g, respectively. POSSOH content: 4.1 wt.%.

The development of such an intricate morphology was of paramount interest. It was decided to more deeply investigate the model system containing both POSSOH and the aluminium catalyst – TM-POSSOH-Al. The system was sampled during the curing cycle, at 6 different times around the gelation time, which was previously determined by rheology (not shown here). The gelation time was close to 40 minutes at 135°C. Sampling consisted in removing specimens from the oven at  $t=0, 20, 30, 40, 50$  and 80 minutes during the dwell at 135°C, and cooling them immediately. All the samples were conserved in the freezer. The two first samples had a glass transition temperature inferior to room temperature and thus were trimmed at low temperature. The evolution of the morphology in the TM-POSSOH-Al system is shown in Figure 2. The morphology was already well defined at the beginning of the dwell at 135°C. The structure in threads seemed to refine in the first 20 to 30 minutes of the dwell

and the final morphology was obtained from 40 minutes, corresponding to the gelation time of this particular system. The threads seemed then to be a result of the evolution of the morphology, initially closer to more classical phase-separated structure in aggregates.

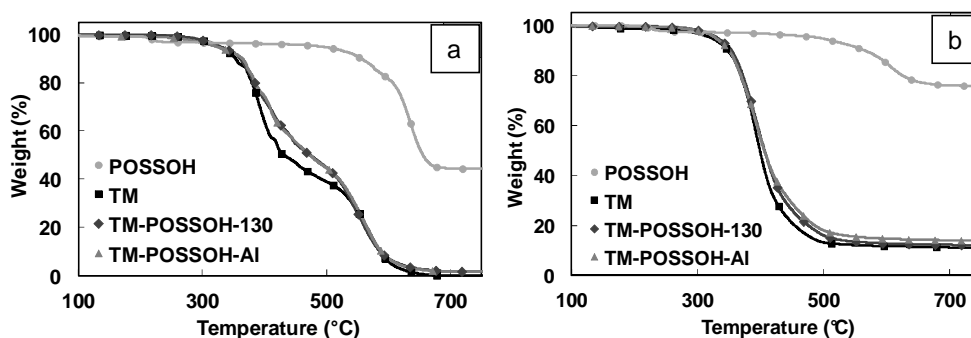


**Figure 2.** Evolution of the morphology of TM-POSSOH-AI during the curing cycle. TEM micrographs at a) t=0 min, b) t=20 min, c) t=30 min, d) t=40 min, e) t=50 min, f) t=80 min, all times referring to the beginning of the dwell at 135°C.

### 3.2. Thermal stability

The thermal stability of TM and MVR444-based networks were assessed by Thermogravimetric Analysis under both air and nitrogen atmosphere. Similar results were obtained for both series of epoxy networks, thus only the results relating to the TM-based networks are displayed (Figure 3).

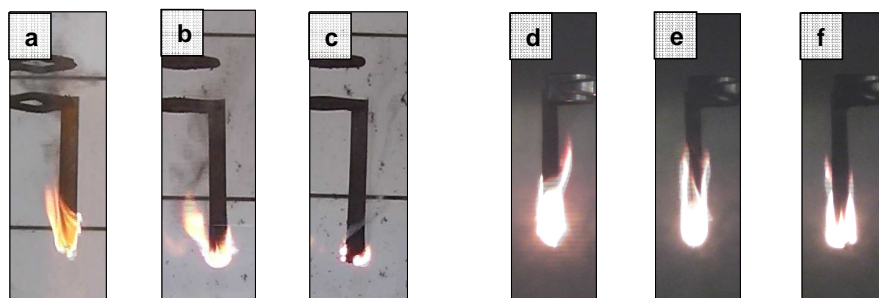
A one-step degradation was observed in nitrogen atmosphere, which was a purely thermal degradation process. Under air atmosphere, the two-step degradation corresponded to the thermal degradation and the oxidation of the product of the first degradation step as usually observed in epoxy networks. Despite the late degradation of neat POSSOH, no effect of its introduction in the networks was observed on temperatures of degradation under nitrogen or air atmosphere. Under air atmosphere, the residues of hybrid networks at the end of the first degradation step were greater of up to 10 wt.% compared to the ones of the epoxy matrices, which revealed a better thermal stability conferred by the POSSOH to the networks until about 500°C. However, the effect of POSSOH on the final residues was purely additional, the values of the residual weights corresponding to the theoretical contribution of the POSSOH.



**Figure 3.** TGA graphs of the TM-based networks under a) air atmosphere and b) nitrogen atmosphere

### 3.3. Fire behaviour

UL-94 tests were performed on the epoxy networks and results are reported in Figure 4 and Table 1. Addition of POSSOH and Al catalyst in the TGDDM-based network brought improvements such as a self-extinguishment about 30 seconds after ignition, a low flame-propagation i.e. an almost undamaged sample at the end of the test. Moreover, no propagation of fire through dripping occurred. The fire behaviour in this particular system was also very stable, as shown by the standard deviations. While the same improvements were not obtained in the MVR-based networks, some characteristic features, observed in the TM-POSS-Al network, were still visible during testing of the MVR-POSSOH-Al samples. In both cases, the area reached by the flame swelled significantly and released gas.

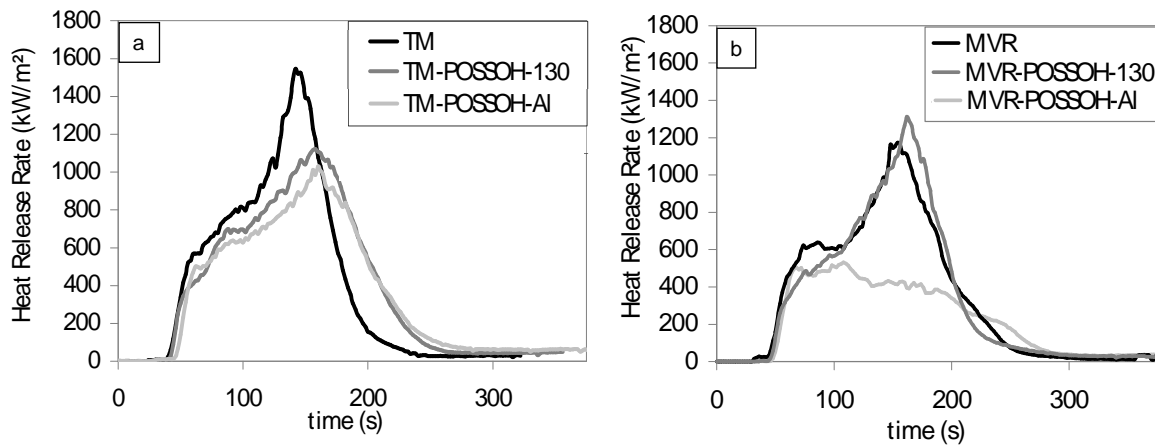


**Figure 4** Pictures of samples during UL-94 at 30 seconds a) TM ; b) TM-POSSOH-130 ; c) TM-POSSOH-Al ; d) MVR ; e) MVR-POSSOH-130 ; f) MVR-POSSOH-Al

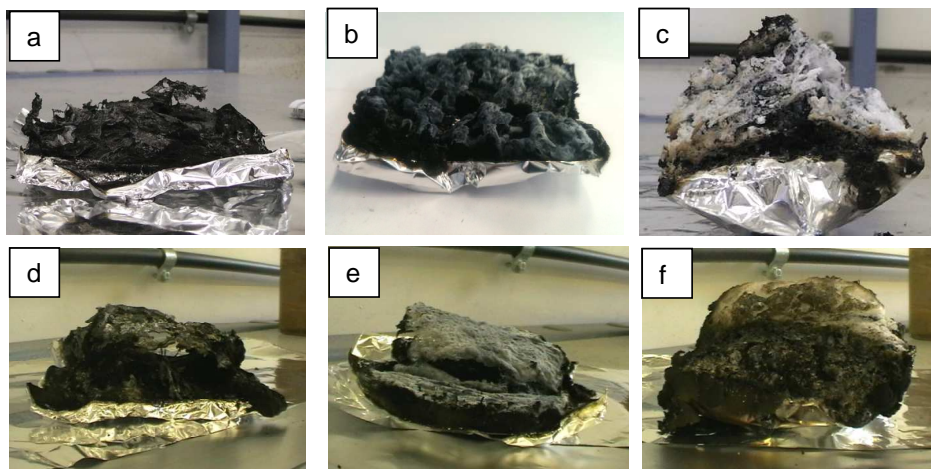
| Networks       | t1<br>(s) | t2<br>(s) | Residual<br>weight<br>(%) | Flame propagation<br>(%) | Ignition of cotton via<br>releasing of flaming drops |
|----------------|-----------|-----------|---------------------------|--------------------------|--|
| TM             | 267       | -         | 5                         | 100                      | 4/4 samples  |
| TM-POSSOH-130  | 234       | -         | 15                        | 100                      | 4/4 samples  |
| TM-POSSOH-Al   | 33        | 13        | 96                        | 12                       | 0/4 samples  |
| MVR            | 194       | -         | 6                         | 100                      | 4/4 samples  |
| MVR-POSSOH-130 | 186       | -         | 18                        | 100                      | 4/4 samples  |
| MVR-POSSOH-Al  | 145       | -         | 59                        | 98                       | 4/4 samples  |

**Table 1** Measurements of times of flaming, residual weight, flame propagation and dripping. Standard deviations are indicated in brackets; t1 and t2 corresponds to the time of flaming after the first and second ignition of the sample, respectively.

Cone calorimeter tests were also carried on all systems, and the HRR curves are displayed in Figure 5. Pictures of the residues after testing are shown in Figure 6, together with the residual weights averaged from 3 tests minimum for each network. Results from the UL-94 tests were confirmed in substance, with the best improvements observed in the case of the POSSOH and Al catalyst-containing networks. The reduction of pHRR and the amount of residue was more important than expected in the MVR-POSSOH-Al network, with a curve shape characteristic of intumescent systems [14]. Indeed, as observed in the UL-94 configuration, the samples containing POSSOH and the Al catalyst significantly swelled under the action of fire, revealing an intumescent behaviour that occurs only in the combined presence of both compounds. Addition of POSSOH alone brought significant reduction of the pHRR but yielded a very low amount of residue in the TM-based network, and seemed even detrimental in the case of the MVR444-based samples, which could not be explained by the authors so far.



**Figure 5** HRR curves of epoxy networks tested with the cone calorimeter ; a) TM-based networks, b) MVR444-based networks



**Figure 6** Cone calorimeter residues of a) TM ; b) TM-POSSOH-130 ; c) TM-POSSOH-Al ; d) MVR ; e) MVR-POSSOH-130 ; f) MVR-POSSOH-Al

#### 4. Conclusion

TrisilanolPhenyl POSS were used, either alone or in combination with an aluminium catalyst, in a model and a commercial epoxy system, used in high-performance applications such as structural parts for aeronautics. The combined presence of both compounds was found to enhance greatly the fire performance and confer a strong intumescent character to the epoxy networks. Even if the UL-94 test and the cone calorimeter allowed to reach the same conclusions in substance, the results strongly depended on the configuration of the test. In particular, mixed results were obtained for the TM-POSSOH system, depending on the test set-up. The purely thermal degradation of the networks was not enhanced significantly by adding the organic-inorganic molecules. The very special morphologies created formed very early during the curing process. No link between these morphologies and the observed fire behaviours could be evidenced so far.

Nevertheless, a system was found that proved to enhance the fire properties of different epoxy systems, independently of their relative complexity. Considering the final application targeted by these systems, the next step of the study will be to evaluate the influence of the presence of fibre reinforcement in such systems.

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