



# Effects of octa(3-chloroammoniumpropyl)octasilsesquioxane on the epoxy self-polymerisation and epoxy–amine curing

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## ABSTRACT

The effect of quaternary ammonium functionalised polyhedral oligomeric silsesquioxane (POSS) on the self-polymerisation of the diglycidyl ether of bisphenol A (DGEBA) and on the DGEBA–Jeffamine-T403 curing was investigated by differential scanning calorimetry. The acidic ammonium groups of POSS were found to catalyze the self-polymerisation of DGEBA but termination reactions severely compete with the propagation and only low conversions in epoxy groups are attained (<20%). A reaction between POSS and DGEBA was revealed at the POSS–matrix boundary suggesting the release of amino functionality of POSS during thermal cure. The catalytic effect of POSS over the epoxy–amine reaction was also demonstrated. The efficiency of this catalytic effect was found to be significantly dependent on the processing conditions.

Finally, two competitive effects were found to affect the glass transition temperature of POSS modified epoxy networks cured under dynamic conditions. It is proposed that the inclusion of POSS at the nanometer scale is responsible for the increase in free volume of the system which results in the depression of  $T_g$ 's while a restriction effect of POSS cages on polymer chain motions (enhanced  $T_g$ 's) is associated to the development of POSS aggregates in the networks with high POSS loadings.

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## 1. Introduction

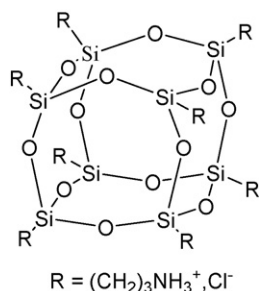
Polyhedral oligomeric silsesquioxanes (POSS) are precisely defined nanobuilding blocks with an inner inorganic cage made up of oxygen and silicon ( $\text{SiO}_{1.5}$ )<sub>n</sub> ( $n=8,10$  or  $12$ ) and externally covered by non-reactive or reactive organic ligands. In that sense, POSS are intrinsically true inorganic–organic hybrid compounds. Polymer organic systems based on cubic POSS have recently attracted considerable interest [1–12]. The nature and functionality of the organic substituents bound to the silicon are generally tuned to increase the compatibility or to generate reactive sites with the polymer matrix. Despite these efforts, it is noteworthy that true nanocomposites (dimensions of phase in the 1–100 nm range) based on POSS have been rarely reported owing to the tendency of POSS to aggregate into amorphous or crystalline domains in the micrometer range. This tendency of POSS to aggregate is more critical with inert POSS or monofunctional POSS rather than with multifunctional POSS, for which steric restrictions around the forming POSS junction limit POSS aggregation [5]. Efficient reinforcement was observed in networks based on DGEBA and poly(oxypropylene)diamine (Jeffamine D2000) with pendant POSS forming crystalline domains which act as physical cross-links

[6]. Therefore, the formation of POSS aggregates with a strong POSS–POSS interaction is not necessarily deleterious in terms of mechanical properties.

Epoxy resins are extensively used as composite matrices, but also as coating materials and adhesives [13]. In the search for advanced epoxy materials with enhanced properties, the preparation of epoxy–POSS nanocomposites with different synthesis strategies has been reported. One of this synthesis approach, developed by Laine and coworkers [7,8] is referred as the nanobuilding block approach. It consists of blending a multifunctional POSS (either epoxy [7] or amino [8] functionalised) with its counterpart reactive component. Well-defined nanocomposites with controlled variation of the organic tether architecture were obtained by changing the compositional ratio or the rigidity and steric hindrance of POSS substituents. Epoxy networks with pendant POSS using monofunctional POSS (either epoxy [5,9–11] or amino [12] functionalised) have also been thoroughly investigated. The synthesis is generally made in two steps: in the first one, a POSS containing one epoxy group (or conversely one amino group) is reacted with an excess of a diamine (or diepoxide resin, respectively). In the second step, this precursor is reacted with the stoichiometric amount of the diepoxide (respectively the diamine). This process did not prevent the phase separation process from occurring in the course of polymerisation, leading to segregated POSS domains in the POSS modified polymer network [10,11]. Epoxy and epoxy–amine blends incorporating octa(3-chloroammoniumpropyl)octasilsesquioxane

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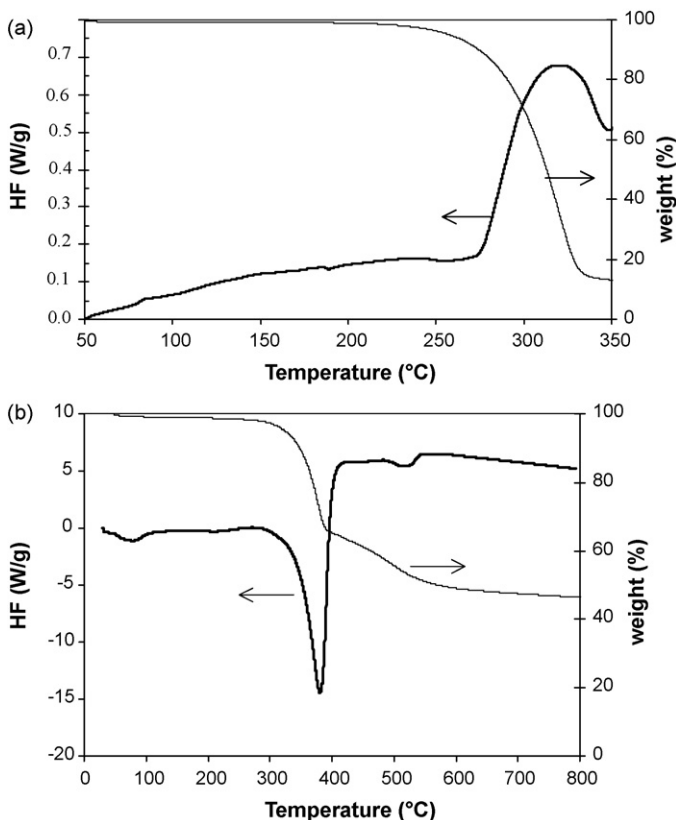
**Scheme 1.** Molecular structure of OCAPS.

(OCAPS) have not been reported before. Our final goal is to prepare OCAPS modified epoxy networks as coatings by a solvent-free route. OCAPS is a quaternary ammonium functionalised POSS (Scheme 1) and, as such, it is water soluble. It also possesses a latent amine functionality that should be more reactive than the aromatic amino groups of octa(aminophenyl)silsesquioxane [8]. Therefore, OCAPS offers a great potential as a modifier of waterborne epoxy networks. The purpose of the present work is to elucidate the effect of OCAPS on the epoxy self-polymerisation and epoxy-amine curing. We will show that the processing conditions exert a significant influence on the reaction advancement and, consequently, on the characteristics of the final material.

## 2. Experimental

### 2.1. Materials

Poly(oxypropylene)triamine (Jeffamine-T403, Huntsman) was used as received. Octa(3-chloroammoniumpropyl)octasilsesquiox-



**Fig. 1.** DSC and TGA thermograms for (a) DGEBA and (b) OCAPS (heating rates of  $10 \text{ K min}^{-1}$ ).

ane was obtained from Hybrid Plastics. Diglycidyl ether of bisphenol A (DGEBA,  $n = 0.15$ ) was slightly heated to melt crystals formed upon storage and then returned to room temperature before mixing with other components. OCAPS was dried under vacuum and stored in a vacuum desiccator over silicagel. All handling of OCAPS was performed under a nitrogen atmosphere to minimize its water uptake before analysis.

### 2.2. Preparation of DGEBA–OCAPS blends

A slurry of DGEBA–OCAPS with 0, 2, 7, 15, 28 and 45 wt% of OCAPS were prepared as follows. OCAPS powder was crushed with a mortar and weighed in test tubes. DGEBA was then added to each individual tube and vigorously stirred with a glass rod.

### 2.3. Preparation of DGEBA/Jeffamine/OCAPS blends

DGEBA/Jeffamine-T403/OCAPS blends with 0, 2, 5 and 7.5 wt% of OCAPS were prepared at a stoichiometric ratio of functional groups  $r(\text{NH/epoxy}) = 1$ . For that calculation, the functionality of OCAPS was taken as  $f = 16$ , that is to say a complete activation of the latent amino reactive groups was considered. The effect of the order of introduction of the reactants was studied by adding OCAPS either to DGEBA or to Jeffamine prior adding the other comonomer.

DGEBA (or Jeffamine-T403) was initially added to the crushed POSS before it underwent a vigorous stirring at room temperature. Jeffamine (or DGEBA) was then poured into the blend and stirred for ca.10 min before analysis.

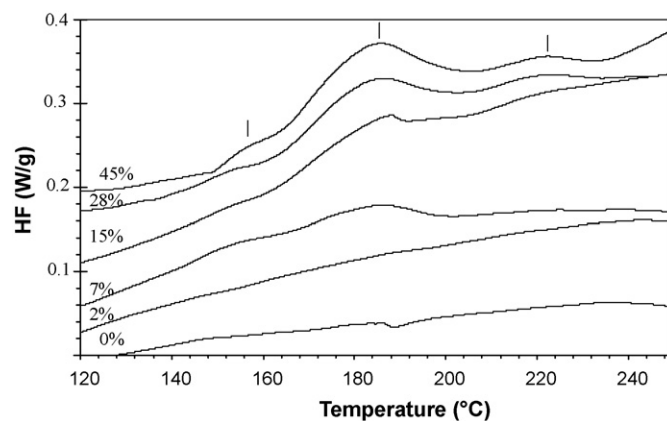
### 2.4. Measurement and techniques

#### 2.4.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were obtained on a Nexus spectrophotometer equipped with a Smart Omni Sampler single reflection ATR system. In all cases, 64 scans at a resolution of  $4 \text{ cm}^{-1}$  were used to record the spectra.

#### 2.4.2. Differential scanning calorimetry (DSC)

The DSC measurements were made with a differential scanning calorimeter (TA Q10 DSC Instrument). The instrument was calibrated for temperature and enthalpy using appropriate reference materials (deuterated chloroform, dodecane, indium and lead). All experiments were conducted under a nitrogen flow (grade 4.5) rate of about  $50 \text{ mL min}^{-1}$  as purge gas. Approximately 5–10 mg samples were weighed accurately and hermetically sealed in DSC aluminum pans. The onset temperature of the exotherm was obtained by extrapolating the steepest portion of the exotherm to the base line.



**Fig. 2.** DSC thermograms of DGEBA–OCAPS blends (heating rates of  $10 \text{ K min}^{-1}$ ). The wt% of OCAPS is indicated on each curve; the scale of heat flow corresponds to 0 wt% OCAPS; the other thermograms have been shifted vertically for clarity.

### 2.4.3. Thermogravimetric analysis (TGA)

TGA was performed on a thermogravimetric analyser Q600 TA Instrument. The measurements were performed over a continuous flow of nitrogen ( $100 \text{ mL min}^{-1}$ ). The samples (4–5 mg) were typically equilibrated at  $30^\circ\text{C}$  and ramped to  $800^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$ .

### 2.4.4. Scanning electron microscopy (SEM)

SEM analysis was carried out with a Phillips XL30 microscope with an energy dispersive X-ray spectroscopy (EDS) probe at an accelerating voltage of 15 kV. Each specimen was coated with a thin layer of gold before analysis.

## 3. Results and discussion

### 3.1. DGEBA–OCAPS blends

DSC and TGA curves for OCAPS and the neat epoxy resins are shown in Fig. 1. The small endotherm between  $40$  and  $100^\circ\text{C}$ , accompanied by a small weight loss ( $\approx 0.8\%$ ), is related to the evaporation of water absorbed by OCAPS during its transfer from the desiccator to the sealed Al pan. This confirms that OCAPS is highly hygroscopic. The temperature of initial degradation, defined as that of 5% weight loss, was  $255^\circ\text{C}$  for DGEBA and  $322^\circ\text{C}$  for OCAPS. OCAPS exhibits a relatively high thermal stability, suggesting that OCAPS modified epoxy networks might possess reasonable stabilities. TGA and DSC of the DGEBA indicate that the thermal degradation of the epoxy becomes significant above  $250^\circ\text{C}$ . The absence of an exothermic event preceding thermal degradation suggests that the self-curing (homopolymerisation) of neat DGEBA does not occur to a significant degree under these conditions. As prepared DGEBA–OCAPS blends were found to be heterogeneous which mirrors the poor compatibility between OCAPS and DGEBA. Heating allows to achieve a more homogeneous state: clear viscous blends were obtained as temperature rises up to  $52$  and  $78^\circ\text{C}$  for the blends with 2 and 7 wt% OCAPS, respectively, suggesting the dissolution of all OCAPS aggregates, at least those in the micrometer range. However, blends with higher POSS contents ( $>15$  wt%) remain translucent during heating suggesting that reactions, if any, will occur in a heterogeneous medium.

The DSC curves for DGEBA–OCAPS blends (Fig. 2) exhibit three weak exotherms near  $158$ ,  $187$  and  $222^\circ\text{C}$ . Remember that no thermal events are recorded in the DSC curves of pure DGEBA and OCAPS in the same temperature range. Alkyl ammonium ions used as cation exchange agents of layered silicate clays were found to catalyze both epoxy homopolymerisation [14] and epoxy–diamine [15] reactions. There is thus a strong suggestion that the first exotherm is related to the homopolymerisation of epoxy catalyzed by the acidic protons of primary ammonium as shown in Eqs. (1)–(3),

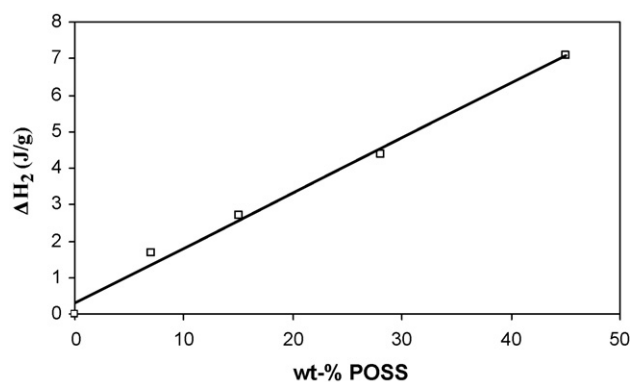
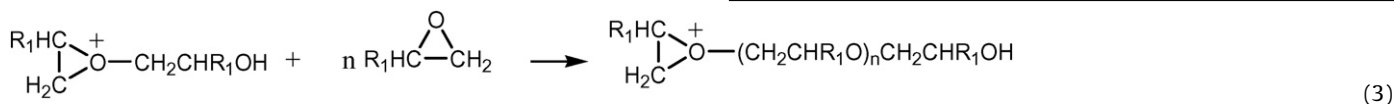
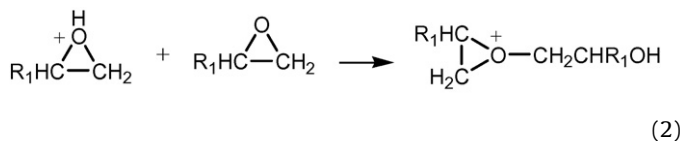
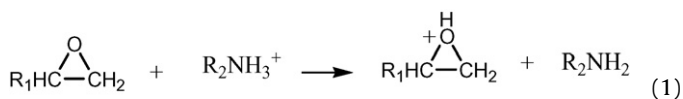


Fig. 3. Plot of the enthalpy of the second exothermic peak versus wt% OCAPS in DGEBA–OCAPS blends.

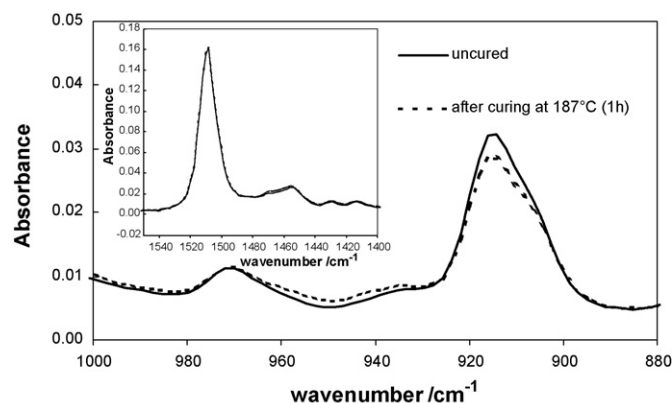


Fig. 4. FTIR spectra of the as prepared DGEBA/OCAPS (28 wt% OCAPS) mixture (solid line) and the same mixture after isothermal heating for 1 h at  $187^\circ\text{C}$  (dashed line). The inset shows the perfect overlap of both spectra in the region of C=C aromatic stretching.

It is clear from Fig. 2 that the intensity of the first exothermic peak is not significantly altered in the blends containing more than 7 wt% OCAPS. In contrast, the intensity of the second exothermic peak increases with increasing OCAPS content. The polymerisation enthalpy associated to the second exothermic peak is indeed linearly related to the OCAPS content in the range 0–45 wt% (Fig. 3). From these observations, it is proposed that the first exothermic event is related to activation by molecularly dispersed POSS catalyst whose concentration remains low and nearly constant above 7 wt% OCAPS content, owing to the poor compatibility between OCAPS and DGEBA. Since the second exothermic event is related to the available POSS surface area, it is believed to be associated to a heterogeneous catalysis of POSS ammonium crystal aggregates. The total polymerisation enthalpy in the temperature range  $140$ – $240^\circ\text{C}$  is low even at high amount of OCAPS ( $<10$  kJ per epoxy equivalent) when it is compared with the  $100$ – $118$  kJ/eq narrow range usually reported for epoxy–amine systems [16]. An epoxy conversion around 16% could be determined from the loss of the oxirane band at  $915 \text{ cm}^{-1}$  for the stoichiometric DGEBA–OCAPS blend (blend with 28 wt% OCAPS) cured at  $187^\circ\text{C}$  for 1 h (Fig. 4). These DSC and FTIR results suggest that only very low molecular weight products are obtained. This is due to the disruption of the polymerisation by different nucleophilic compounds (chloride counter-ions, free amine groups of OCAPS, and alcohol hydroxyls) that compete with DGEBA monomer for the oxonium ions (Eq. (3)).

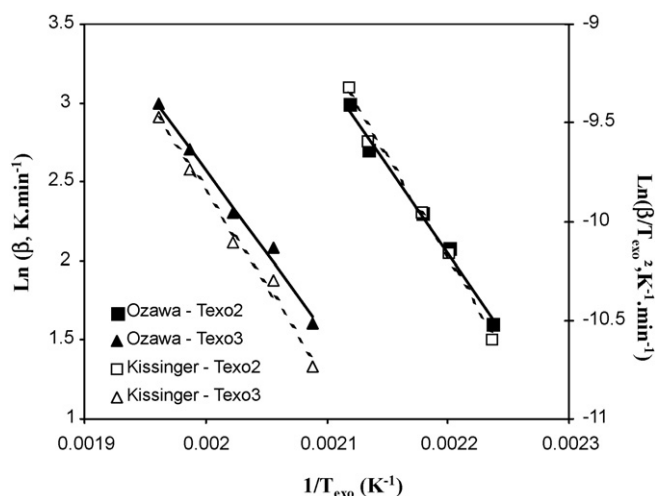


Fig. 5. Plots for the determination of  $E_a$  by Kissinger and Ozawa methods for the DGEBA-OCAPS (28 wt%) blend.

The intensity of the third exothermic event also slightly increases with the OCAPS content but its origin remains unclear. This small thermal event could be related to the etherification reaction between hydroxyl groups and the oxirane rings. From Eqs. (1) and (2), it is clear that the build up of hydroxyl groups should increase with the OCAPS content. In the absence of a basic catalyst (such as a tertiary amine), this etherification reaction occurs only at temperatures above 200 °C [17].

Kissinger and Ozawa methods [18,19] were applied to calculate activation energy ( $E_a$ ) for the polymerisation processes involved in the DGEBA-OCAPS blends. Kissinger's equation can be expressed as follows

$$\ln\left(\frac{\beta}{T_{\text{exo}}^2}\right) = -\frac{E_a}{RT_{\text{exo}}} + \ln\frac{AR}{E_a} \quad (4)$$

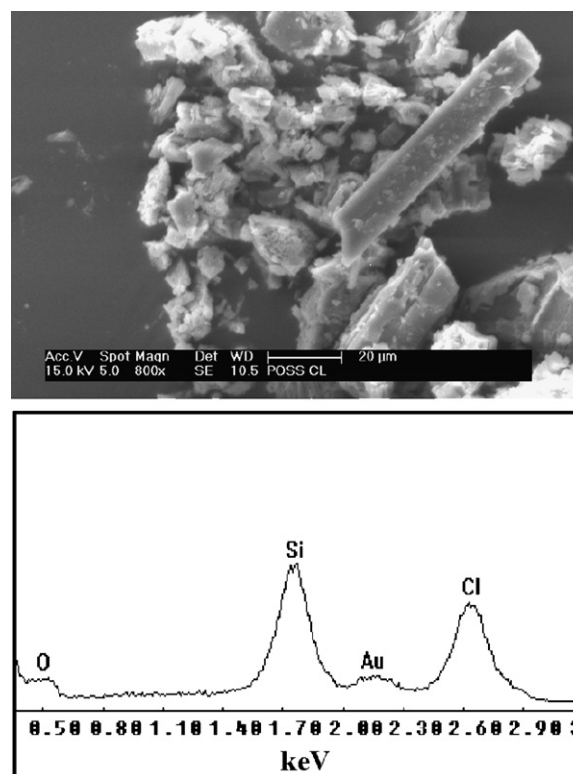


Fig. 6. SEM micrograph of OCAPS. The accompanying EDS spectrum is below.

where  $\beta$ ,  $T_{\text{exo}}$ ,  $A$  and  $R$  are the heating rate, the temperature at the exotherm maximum, the frequency factor and the gas constant. Therefore,  $E_a$  could be obtained from the slope of  $\ln(\beta/T_{\text{exo}}^2)$  vs  $1/T_{\text{exo}}$  plot (Fig. 5).

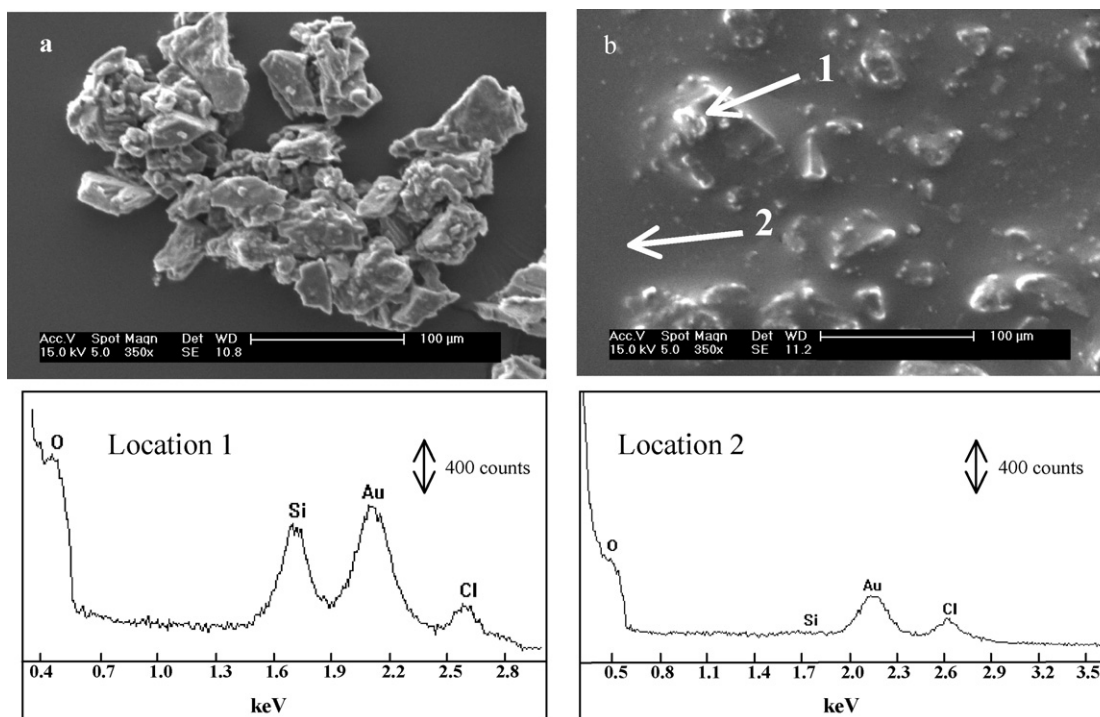


Fig. 7. Representative SEM micrographs of DGEBA/OCAPS blends (72:28 wt%) treated for (a) 1 h at 158 °C or (b) 1 h at 187 °C and representative EDS spectra collected at the POSS-matrix interface (point 1 in b) and in a free POSS region (point 2 in b) of the 187 °C treated sample.

Ozawa's equation gives

$$E_a = -\frac{R}{1.052} \times \frac{d \ln \beta}{d(1/T_{\text{exo}})} \quad (5)$$

and, therefore,  $E_a$  could be obtained from the slope of  $\ln(\beta)$  vs  $1/T_{\text{exo}}$  plot (Fig. 5).

Dynamic DSC data were performed at 5, 8, 10, 15 and 20 K min<sup>-1</sup>. The activation energy associated to the first exotherm was not determined because it appears as a broad and low shoulder signal on the DSC curve. The values of  $E_a$  associated to the second exotherm from the Kissinger and Ozawa methods are 84.4 and 87.5 kJ mol<sup>-1</sup>, respectively. The values of  $E_a$  associated to the third exotherm from the Kissinger and Ozawa methods are 79.1 and 83.0 kJ mol<sup>-1</sup>, respectively. These values are within the same range as the  $E_a$  values of acid-catalyzed self-polymerisation of DGEBA by the alkylammonium ion exchanged forms of montmorillonite [20].

The SEM image (Fig. 6) of OCAPS powder shows angular POSS particles and microvoids with size ranging from 1 to 80 μm. The EDS spectrum (Fig. 6) includes the Si and Cl elements at an approximately equal atomic ratio irrespective of the location of the area selected for EDS analysis (50 ± 2 wt%). This corresponds to the theoretical calculation in the proposed structure of OCAPS.

SEM-EDS results on the stoichiometric DGEBA/OCAPS blend (72:28 wt%) after 1 h isothermal treatments at 158 or 187 °C are shown in Fig. 7. POSS aggregates are found to be only slightly affected by the treatment at 158 °C while they are enwrapped by the epoxy resin after the cure at higher temperatures. The 158 °C cured samples yielded EDS spectra such as that shown above in Fig. 6, giving Si:Cl ratio near unity, whatever be the location of the EDS analysis (the reader is reminded that EDS samples are about 4 μm below the surface).

On the contrary, dramatic differences were noted between the EDS spectra in the POSS-matrix boundary and the one in the matrix rich region after the cure at 187 °C. Some matrix rich areas (as location 2 in Fig. 7b) were found to be free of POSS (no Si element) but contained a low amount of Cl element. EDS analysis at the proximity of the POSS-matrix interface (as location 1 in Fig. 7b) typically resulted in a Si:Cl ratio far higher than unity, which confirms the catalytic homopolymerisation of DGEBA by primary ammonium of POSS crystals. At these relatively high cure temperatures, it may be anticipated that amino groups reacted with oxirane groups or with the tertiary oxonium ions and thus, that they are bonded to the epoxy resin. Note that a cure for 1 h at 222 °C gave the same SEM and EDS features than the 187 °C cure (not shown for brevity).

### 3.2. DGEBA/Jeffamine/OCAPS blends

The synthesis of POSS modified epoxy-Jeffamine network was performed by pre-mixing OCAPS and DGEBA or OCAPS and Jeffamine before adding the third component of the blend. The blends were prepared to lead to an overall stoichiometric proportion of epoxy and NH functionalities by considering that OCAPS is a latent hardener with a functionality of 16 (this assumption will be discussed later on). DSC thermograms of the as prepared blends with a 5 wt% OCAPS are shown in Fig. 8. A broad curing exotherm was observed in all the samples. The POSS based blends exhibit a significantly lower onset temperature ( $T_{\text{onset}}$ ) of the exotherm than the DGEBA-Jeffamine network. This suggests that the acidic ammonium groups of OCAPS might catalyze the epoxy-amine reaction by forming an intermediate ammonium-epoxy complex. The possibility of catalysis by residual water in the hydrophilic POSS was ruled out by performing DSC analysis of a DGEBA-Jeffamine blend with 0.1 wt% water (which is far greater than the actual one): the onset of the exotherm was found to be not appreciably shifted to lower temperature compared to the DGEBA-Jeffamine blend. Interestingly, the formulation prepared by pre-mixing OCAPS and DGEBA fol-

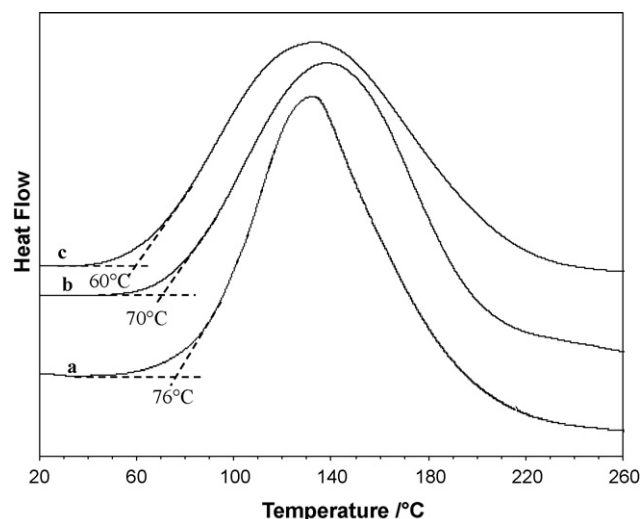


Fig. 8. DSC thermograms (first DSC scan) of DGEBA-T403 ( $r=1$ ) blends without (a) and with 5 wt% OCAPS (b and c). POSS based blends were prepared by pre-mixing OCAPS with T403 (b) or with DGEBA (c) before adding the third component (curves shifted vertically for clarity).

lowed by subsequent addition of Jeffamine exhibit a shift in  $T_{\text{onset}}$  of -16 °C while the formulation prepared by pre-mixing OCAPS and Jeffamine followed by subsequent addition of DGEBA exhibit a shift of only -6 °C. Thus, it looks as if Jeffamine chains around POSS particles in the pre-mixing step would partly hinder the formation of the ammonium-epoxy complex. Upon second ramp, all the specimens show no additional exothermic event and only a broad transition associated to the  $T_g$  was observed (Fig. 9). From DSC results of DGEBA-OCAPS blends, it was found that the reaction between the latent amino groups of OCAPS and epoxy groups is scarce, occurs at temperatures above 150 °C and is mostly interfacial in nature. That is to say, OCAPS contributes poorly to the NH functionality of the blends. Therefore, the actual ratio,  $r$ , between the amino and epoxy groups was recalculated taking OCAPS as an inert filler:  $r$  values of 0.71, 0.81 and 0.92 were found for blends with 7.5, 5 and 2 wt% of OCAPS, respectively. DGEBA-Jeffamine blends with  $r=0.71$ , 0.81 and 0.92 were prepared as non-POSS parent networks to give a more precise understanding of the role of OCAPS in the  $T_g$  of the networks. The  $T_g$  values are shown in Table 1. The  $T_g$  values increase with the amount of OCAPS for a given order of mixing reactants. The POSS based networks with 2 wt% POSS have a  $T_g$  which is lower than the  $T_g$  of the non-POSS parent network. From this, it appears that POSS cubes are not efficiently integrated as network junctions units and, consequently, a diluent role of the

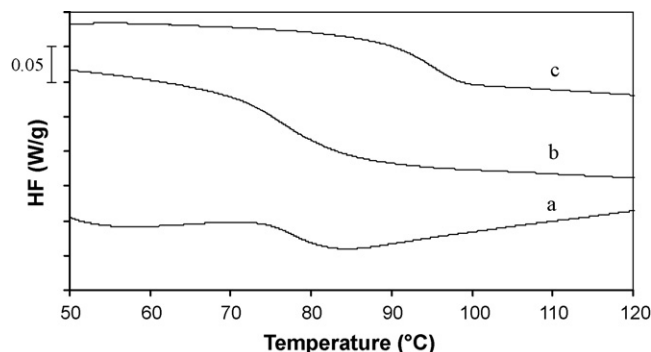


Fig. 9. DSC thermograms (second DSC scan) of DGEBA-T403 ( $r=0.81$ ) blend without OCAPS (a), (b) and (c): same as (a) with 5 wt% OCAPS. POSS based blends prepared by pre-mixing OCAPS with T403 (b) or with DGEBA (c) before adding the third component (curves shifted vertically for clarity).

**Table 1**  
Glass temperature  $T_g$  for selected networks.

Sample <sup>a</sup>	$r = (\text{NH: epoxy})^b$	wt% of OCAPS	$T_g^c$ (°C)	$\Delta T_g^d$ (°C)
DGEBA–T403	1	0	92.7 (9.3)	–
DGEBA–T403	0.92	0	91.1 (9.5)	–
DGEBA–T403	0.81	0	78.0 (8.2)	–
DGEBA–T403	0.71	0	69.5 (11.7)	–
DGEBA–(T403–OCAPS)	0.92	2	76.8 (13.8)	–14.3
DGEBA–(T403–OCAPS)	0.81	5	78.7 (18.3)	+0.7
DGEBA–(T403–OCAPS)	0.71	7.5	85.5 (14.0)	+16.0
(DGEBA–OCAPS)–T403	0.92	2	88.2 (14.1)	–2.9
(DGEBA–OCAPS)–T403	0.81	5	94.1 (8.7)	+16.1
(DGEBA–OCAPS)–T403	0.71	7.5	94.6 (8.2)	+25.1

<sup>a</sup> DGEBA–(T403–OCAPS) blends prepared by pre-mixing T403 and OCAPS followed by addition of DGEBA and (DGEBA–OCAPS)–T403 blends prepared by pre-mixing DGEBA and OCAPS followed by addition of T403.

<sup>b</sup> For POSS based blends, the reported  $r$  values consider OCAPS as an inert filler (i.e., ammonium groups are not activated to give nucleophilic amino groups during thermal cure).

<sup>c</sup>  $T_g$  taken as the midpoint of the step transition; the breadth of the glass transition is indicated in bracket.

<sup>d</sup> Difference between the  $T_g$  of the POSS based network and the  $T_g$  of the POSS free network with the same  $r$  value.

molecularly dispersed POSS cubes might predominate at a relative low content of POSS (2 wt%). At a higher POSS content (>5 wt%), the POSS based networks exhibit a higher  $T_g$  than the non-POSS parent network. Particularly, the networks prepared by premixing OCAPS with DGEBA followed by addition of Jeffamine exhibit a  $T_g$  near the  $T_g$  of a stoichiometric epoxy–amine network. Therefore, another role of POSS predominates at these high POSS fractions. At this stage, the exact mechanism that explains the rise in  $T_g$  with the POSS content is not clear. The rise in  $T_g$  is apparently associated to a rise in the heterogeneity in the POSS modified network. Segregated POSS domains could form physical cross-links or occluded matrix in POSS aggregates that could give rise to enhanced  $T_g$ 's. However, it must be borne in mind that polyetherification reaction will become increasingly more important as the POSS content (and epoxy excess) increase, which will affect the  $T_g$  of the final network.

Another interesting result is that pre-mixing DGEBA and OCAPS before adding Jeffamine always gives networks with higher  $T_g$  than the networks prepared by pre-mixing Jeffamine and OCAPS before adding DGEBA. Jeffamine chains would interact with OCAPS to create a sort of steric hindrance (i) for the formation of DGEBA–OCAPS complex responsible for the catalytic effect of OCAPS over the epoxy–amine reaction and/or (ii) for the interfacial reaction between OCAPS and epoxy. That would explain the smaller values of  $T_g$ 's when Jeffamine is pre-mixed with OCAPS.

#### 4. Conclusion

In conclusion, we have demonstrated that octaammonium POSS catalyzes the epoxy–amine reaction between DGEBA and Jeffamine–T403. The octaammonium POSS also catalyzes the homopolymerisation of DGEBA but the latter reaction occurs at a significant higher temperature ( $T_{\text{onset}}$  near 150 °C) than the epoxy–amine reaction ( $T_{\text{onset}}$  near 60 °C). SEM–EDS results showed that POSS and the epoxy react at the POSS–DGEBA boundary,

demonstrating the release of amino functionality during thermal curing of POSS–DGEBA blends. POSS cubes were found to play opposing roles over the molecular mobility of DGEBA–T403 networks that result in a lowering of  $T_g$  at low POSS content and a rise in  $T_g$  at high POSS fractions. OCAPS, as an octa(ammonium chloride) salt, is water soluble and, as such, can be readily incorporated as a modifier of waterborne epoxy coatings; research that we are currently undertaking.

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