Octasilsesquioxane reinforced DGEBA and TGDDM epoxy nanocomposites:

Characterization of Thermal, Dielectric and Morphological properties Shanmugam Nagendiran[†], Muthukaruppan Alagar^{†,*} and Ian Hamerton[§] [†]Department of Chemical Engineering, Anna University, Chennai 600 025, India. [§]Chemical Sciences Division, Faculty of Health and Medical Sciences, University of

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Abstract:

The octa-functionalized polyhedral oligomeric silsesquioxane (POSS) containing nanocomposites of epoxy resin are prepared via in situ co-polymerization of epoxy resins with 4,4'-diaminodiphenylsulfone (DDS) in the presence of octaaminophenyl silsesquioxane (OAPS). Two of the most common, technologically relevant epoxy resins, diglycidyl ether of bisphenol-A (DGEBA) and tetraglycidyl diamino diphenyl methane (TGDDM) are studied and the organic-inorganic hybrid nanocomposites containing up to 20 wt% of OAPS are obtained. The curing reaction involving epoxy, DDS and OAPS is investigated using Fourier transform infrared (FT-IR) spectroscopy. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) show that the glass transition temperature (T_g) of the POSS containing nanocomposites are higher than the corresponding neat epoxy systems at lower concentrations of POSS ($\leq 3 \text{ wt\%}$). For the POSS-epoxy nanocomposites, the storage moduli of the rubbery plateau are higher than that of the neat epoxy when the resins contain less than 20 wt% POSS, indicating the nanoreinforcement effect of POSS cages. Thermogravimetric analysis (TGA) indicates that the POSS containing epoxy nanocomposites display high ceramic yields, suggesting the flame retardant behaviour of the materials is improved. The increasing concentration of OAPS into epoxy-amine networks exhibit a decreasing trend in the values of dielectric constant compared with those values obtained from neat epoxy systems. The higher epoxy functionality present in TGDDM leads to nanocomposites which possess enhanced thermal stability and higher dielectric constants than the DGEBA-based nanocomposites. X-ray diffraction (XRD) analysis reveals that the molecular level reinforcement of POSS cages occurrs in both the cases of DGEBA- and TGDDM-based hybrid epoxy nanocomposites. Furthermore, homogeneous dispersion of POSS cages in the epoxy matrices is evidenced by scanning electron microscopy (SEM) which further confirms that the POSS molecule has become an integral part of the organic-inorganic inter-crosslinked network systems.

Keywords: DGEBA and TGDDM epoxy resins; POSS; Nanocomposites; Thermal and Dielectric properties

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1. Introduction

Polymer systems that are reinforced with well-defined, nanosized inorganic clusters have been attracting considerable interest recently due to their potential application in a wide variety of technological areas [1-5]. The nanoscaled distribution of reinforcing agents can optimize the interactions between different molecular components and can afford materials with improved properties [6,7]. Cubic structured polyhedral oligomeric silsesquioxane (POSS) reagents are typical molecular

nanobuilding blocks that are used to reinforce the organic polymer matrix. The cagelike structures of POSS can allow the construction of materials with precise control over the nanoarchitecture. They combine a hybrid inorganic-organic composition with cage structures that have comparable dimensions to those of most polymeric segments. Consequently, POSS reagents, monomers and polymers are emerging as a new chemical technology for the preparation of nanoscaled organic-inorganic hybrids [6,7] and the polymers comprising POSS skeletons are becoming the focus of many studies due to their ease of processing and their excellent and comprehensive range of properties [8,9].

POSS molecules are typically derived from the hydrolysis and condensation of trifunctional organosilanes and possess the general formula $R_n(SiO_{1.5})_n$, where n = 6 - 12 and where R denotes various organic residues of which one (or more) is reactive or polymerizable. The cubic silica cores are completely defined as 'hard particles' with a 0.53 nm diameter and a spherical radius of 1–3 nm including peripheral organic (R) units. Generally, POSS cages can be incorporated into polymers *via* copolymerization and/or physical blending, although the copolymerization is a particularly efficient approach to the formation of nanocomposites since covalent bonds result between the POSS cages and the organic polymer matrices. Furthermore, it has been reported that some nanocomposites prepared *via* physical blending [10] have displayed immiscibility between the silsesquioxane and the organic polymer matrix, an undesirable drawback.

Epoxy resins are among the most commercially successful commercial polymers known, and they have been widely used as coatings, adhesives, structural materials and electronic encapsulating materials due to their efficient bonding, high modulus and strength, excellent chemical resistance and simplicity in processing. The extensive applications of epoxy resins have paved an avenue to prepare organicinorganic hybrid nanocomposites with improved properties. There have been several reports of organic-inorganic nanocomposites involving epoxy resin and POSS during the past few years [11-14] and this modification can endow the materials with superior properties such as improved thermo-mechanical, thermal, flame retardance and dielectric properties [15-17]. For example, Lee and Lichtenhan [18] have investigated the properties of thermal and viscoelastic enhancements in commonly used epoxy resins reinforced with monofunctional POSS-epoxy macromers and the experiments performed under identical thermodynamic states revealed that the molecular level reinforcement provided by the POSS cages also retarded the physical ageing process in the glassy states. Similarly, Laine et al. [14, 19-21] studied and compared the properties of epoxy resins with reinforcement of different functionalized POSS. While Fu et al. [22] reported the important finding that the addition of small amount of POSS into an epoxy resin did not appear to increase the viscosity of the mixture significantly nor accelerate the reaction during the pregelation stage. Recently, Zheng et al. [23,24] evaluated the effect of the type and reactivity of functional groups in POSS cages on the phase behaviour and thermomechanical properties in the resulting DDM cured epoxy hybrids.

In the present work, we report the influence of octa-amino functionalized POSS, *i.e.* OAPS, on the thermal, dielectric and morphological properties of DDS cured epoxy hybrid nanocomposites (incorporating either DGEBA or TGDDM). The final properties of the nanocomposites were investigated by a variety of means including differential scanning calorimetry (DSC), dynamic mechanical analysis

(DMA), thermogravimetric analysis (TGA), impedance analysis, X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM) and details of the analytical procedures are given below.

2. Experimental

2.1 Materials

Two conventional and industrially important epoxy resins were used in the present study, diglycidyl ether of bisphenol A, DGEBA (LY556, equivalent epoxide [E] weight: 185-190 g mol.) and tetraglycidyl diamino diphenyl methane, TGDDM (equivalent [E] weight: 105.5 g mol.) were purchased from Ciba-Geigy Ltd., (India) and Aldrich (USA), respectively. The epoxies were cured with 4,4'- diaminodiphenylsulfone (DDS) obtained from Lancaster, India. Phenyltrichlorosilane (PhSiCl₃, 98%) and 5 wt% Pd/C were also purchased from Lancaster, India. Benzyltrimethylammonium hydroxide (40% in methanol solution), formic acid (98%), tetrahydrofuran (THF) and triethylamine (TEA) were purchased from SD Fine chemicals, India. THF and TEA were used after drying with Na/benzophenone and KOH respectively. Other chemicals were used as purchased.

2.2 Synthesis of Octaphenylsilsesquioxane (OPS)

The OPS was synthesized in a manner reported by Huang *et al.* [25]. In this way, Phenyltrichlorosilane (10.9 g, 0.05 mol.) was dissolved in benzene (50 cm³) and shaken with distilled water (100 cm³) for 5 h at 25 °C. After removing the aqueous layer, the organic layer was washed with water until neutral and dried with anhydrous magnesium sulphate. To this organic layer, 1.2 ml (3 mmol.) of 40% benzyltrimethylammonium hydroxide/methanol solution was added and refluxed for 4

h, then allowed to stand for 4 days. The mixture was refluxed again for another 24 h and cooled and then filtered to give white microcrystalline powder. The product thus obtained was extracted, using dry benzene in a Soxhlet extractor to remove the soluble resin and further dried in vacuum at 70 °C to yield 6.0 g (5.8 mmol., 91.5%). FTIR (cm⁻¹) with KBr powder: 3073, 1630, 1136; solid ²⁹Si NMR (ppm): - 79.4; Anal. Calc. for Si₈O₁₂C₄₈H₄₀: C 55.78%, H 3.90%; Found, C 55.62%, H 4.10%.

2.3 Synthesis of Octa(nitrophenyl)silsesquioxane (ONPS)

The ONPS was synthesized by following Laine's method [<mark>6</mark>]. Octaphenylsilsesquioxane (OPS) (10 g, 9.7 mmol.) was added in small portions to fuming nitric acid (60 cm³) with stirring at 0°C. When the addition was completed, the solution was stirred at 0°C for an additional 30 minutes and then at room temperature for 20 h. After filtration through glass wool, the solution was poured on to ice (100 g). A very faintly yellow precipitate was collected by filtration and washed with water (5 x 50 cm³) until pH = 6.0 and then with ethanol (2 x 50 cm³). The resulting powder was dried under vacuum at ambient temperature to remove residual solvent to yield 12.02 g (8.6 mmol., 89.2%) of material. FTIR (cm⁻¹) with KBr powder: 3074, 1610, 1530, 1350, 1096; ¹H-NMR (acetone-d₆ ppm): 8.6 (t, 1H), 8.5-8.0 (m, 4.1H), 7.8(m, 2.8H); ¹³C-NMR (acetone-d₆, ppm): 154.0, 149.0, 141.1, 138.7, 135.5, 134.3, 132.3, 131.0, 129.6, 127.2, 125.3; ²⁹Si-NMR (ppm): -79.8, -83.0; GPC M_n 1168 g mol.⁻¹, M_w 1204 g mol.⁻¹, PDI = 1.03. Anal. Calc. for Si₈O₂₈N₈C₄₈H₃₂: C 41.37%, H 2.31%, N 8.04%; Found, C 41.50%, H 2.15% and N 8.12%.

2.4 Synthesis of Octa(aminophenyl)silsesquioxane (OAPS)

ONPS (10.0 g, 7.16 mmol.) and 5 wt % Pd/C (1.22 g, 0.574 mmol.) were placed into a 250-ml RBF equipped with a condenser under N₂. Distilled THF (80 cm³) and triethylamine (80 cm³, 0.574 mol.) were then added and the mixture was heated to 60 °C, and 98% formic acid (10.4 cm³, 0.230 mol.) was added slowly at 60 °C. After the addition of formic acid (4.6 cm^3) to the reaction mixture, a dark yellow colour was observed which then gradually disappeared by the slow addition of remaining formic acid. During the addition of formic acid, carbon dioxide evolved and the solution separated into two layers. After 5 h, the THF layer was separated, and THF (50 cm^3) and water (50 cm^3) were added until the slurry formed a black suspension. The suspension and THF solution separated previously were mixed together and filtered through Celite. Further portions of THF (20 cm^3) and water (20 cm^3) cm³) were added to the flask to dissolve the remaining black slurry, and the suspension was filtered again. All the THF filtrates were combined with ethylacetate (50 cm³) and washed with water (4x 100 cm³). The organic layer was dried with $MgSO_4$ (5 g) and precipitated by addition of hexane (2 dm³). A white precipitate was collected by filtration, redissolved in 30:50 THF/ethylacetate and reprecipitated into hexane (1 dm^3) . The powder thus obtained was dried under vacuum to yield 6.2 g (5.44 mmol., 76%). FTIR (cm⁻¹) with KBr powder: 3391, 1621, 1121; ¹H-NMR (acetone-d₆ ppm): 7.6-6.5 (b, 11.3H), 5.0-3.9 (b, 5.8H); 13 C-NMR (acetone-d₆ ppm): 153.8, 147.9, 136.4, 132.6, 126.2, 123.6, 120.7, 117.3, 115.7, 114.3; ²⁹Si-NMR (ppm): -77.97 (shoulder peak), -79.14. GPC M_n 1058 g mol.⁻¹, M_w 1094 g mol.⁻¹, PDI = 1.04. Anal. Calc. for Si₈O₁₂C₄₈N₈H₄₈: C 49.97%, H 4.19%, N 9.71%; Found, C 50.1%, H 4.13% and N 9.65%.

2.5 Preparation of Nanocomposites

In order to prepare the composites of epoxy resins with OAPS, the latter was first dissolved in the smallest possible amount of THF and the solution was mixed with the desired amount of DGEBA or TGDDM at 25 °C. The mixture obtained was heated to 60 °C with continuous stirring to evaporate the majority of solvent and then degassed under vacuum at 60 °C to remove the residual solvent. Subsequently, the stoichiometric amount of curing agent (DDS) was added into the molten epoxy at 120°C and stirred continuously until an homogeneous, transparent solution was formed. After degassing, the mixture was poured into a Teflon coated iron mould. It was thermally cured: first at 140 °C (4 hrs) before the temperature was raised slowly to 200°C and then maintained at this temperature (3 hrs) for the curing reaction to reach completion.

2.6 Characterization

FTIR spectra were recorded on a Perkin–Elmer 6X FTIR spectrophotometer; samples were presented as KBr pellets. ¹H NMR, ¹³C NMR and ²⁹Si NMR spectra were collected on a Jeol GSX 400 MHz spectrometer using acetone-d₆ as solvent and tetramethylsilane (TMS) as internal standard. GPC analysis was performed using Waters GPC system with Waters 410 RI detector. The system was calibrated using polystyrene standards and THF was used as the eluent, at a flow rate of 1.0 cm³ min.⁻¹ The glass transition temperatures (T_g) of the nanocomposites were characterized using a Netzsch DSC-200 differential scanning calorimeter. Dynamic mechanical analysis (DMA) measurements were performed in a N₂ atmosphere using a NETZSCH DMA 242 at a heating rate of 5 K min.⁻¹ and a frequency of 10 Hz. The thermal stability was characterized using a Netzsch STA 409) thermogravimetric analyzer at a heating rate of 10 K min.⁻¹ in a nitrogen atmosphere. The dielectrical properties of the neat and the POSS modified systems were tested with the help of impedance analyzer (Solartron impedance/gain phase analyzer 1260) at RT using Platinum (Pt) electrode in the frequency range at 1 MHz. Water absorption property was determined by swelling the samples in distilled water for 7 days at 30 °C. The X-ray diffraction analysis was studied using a Rich Seifert-3000 X-ray diffractometer over the 2θ range of 5-60° at a scanning rate of 0.04°/min. Scanning electron microscopy (Jeol JSM-6360) was used to study the morphology of the nanocomposites at the gold coated cross-section area.

3. Results and Discussion

3.1 Structure of POSS

OAPS was synthesized in a three-step reaction. The first step involved in the synthesis of OPS *via* the hydrolysis and condensation of phenyltrichlorosilane and the subsequent rearrangement reaction catalyzed by benzyltrimethylammonium hydroxide according to Huang's method [25]. The second and third steps were nitration of OPS *i.e.* to form ONPS and hydrogen-transfer reduction of ONPS to OAPS (Scheme 1) respectively according to Laine's method [6]. FTIR, ¹H, ¹³C and ²⁹Si NMR spectra of all the POSS monomers are shown in Figs. 1-3. Formation of *meta* and *para* isomers and cage retention in OAPS were supported by these data. Furthermore, the FTIR spectra and ¹H NMR spectra of ONPS and OAPS indicated a complete conversion of nitro groups to amino groups. In the FTIR spectrum of OAPS, the peaks at 1353 and 1531 cm⁻¹ (v N=O) disappear while a new broad peak at 3390 cm⁻¹ (v N-H) is observed (Fig. 3(a)). Likewise, in the ¹H NMR spectrum of OAPS, the aromatic peaks of ONPS disappeared completely to be replaced by new aromatic peaks at lower magnetic field (Fig. 3(b)). Ten primary peaks corresponding to ten

different carbon environments of both isomers were observed in the ¹³C NMR spectrum of ONPS (Fig. 2(c)) with one small peak [6], and ten peaks were also observed in the ¹³C NMR spectrum of OAPS (Fig. 3(c)). For the ¹H NMR spectrum of ONPS, no peak was observed above 9.0 ppm and this confirmed the absence of the dinitro compound per aromatic group. The resonance of aromatic protons in ¹H NMR spectrum is observed to split into three at 8.7, 8.5-8.0 and 7.8 ppm, respectively, implying that the ONPS could be the combined isomers containing para- and metaposition substitutions. In Fig. 2(d), two peaks observed in ²⁹Si NMR at -79.8 and -83.0 ppm for ONPS and the peaks at -77.9 ppm (shoulder peak) and -79.1 ppm for OAPS (Fig. 3(d)) suggesting that only two isomers are formed whereas a single peak was observed at -79.4 °C for OPS (Fig.1(b)). Furthermore, the absence of the ortho isomer because of steric hindrance is confirmed from ²⁹Si NMR data. In the ¹H NMR spectrum of OAPS, the integration ratio of peaks corresponding to the amino groups and the aromatic groups equates to 1:2. These results indicate that both isomers have eight nitro groups or amino groups. The triplet peaks at 8.7 ppm were assigned to protons between the nitro group and the siloxy group in the meta isomer. The cage structure of OPS, ONPS and OAPS are confirmed by ²⁹Si NMR spectra, because only peaks assigned to cubic silicon appear in all the ²⁹Si NMR spectra. The narrow polydispersity indices of ONPS and OAPS provided by GPC data also confirm the retention of the cage structure.

3.2 FT-IR spectral analysis of nanocomposites

Figs. 4(a) and 4(b) show the FTIR spectra of neat and nanocomposite systems, from which it is clearly seen that the epoxy stretching frequencies at

914.1 cm⁻¹ for the DGEBA epoxy and a peak at 906.7 cm⁻¹ for the TGDDM epoxy are absent in the DDS cured epoxy systems (both the DGEBA and TGDDM) as well as their POSS reinforced nanocomposites. The disappearance of the epoxy peak in the neat and nanocomposite systems indicated that the complete cure had occurred in both the DGEBA and TGDDM epoxy based systems. The appearance of Si-O-Si peak at $\sim 1100 \text{ cm}^{-1}$ and the Si-C peak at 1180 cm⁻¹ from the spacer groups, which appeared in the POSS reinforced epoxy nanocomposites, confirmed the presence of POSS in those systems as neither are present in the pure epoxy and DDS cured epoxy resins. The overlay of O-H stretching generated from the curing of epoxy resin systems is also observed at 3200- 3500 cm⁻¹. The peaks at ~1500 cm⁻¹ and ~1600 cm⁻¹ showed the aromatic -C=C- stretching bands which gradually increased with incorporation of OAPS into the epoxy resins. The sharp N-H stretching peaks at 3338 cm⁻¹ and 3364 cm⁻¹ in DDS, which are absent in all the DDS cured epoxy systems as well as their POSS nanocomposites, clearly indicate that as expected the amine is involved in the ring opening polymerization of DGEBA and TGDDM epoxy resins.

3.3 Glass transition behaviour

DSC measurements were performed for the epoxy-amine networks containing multifuntional POSS as a nanoreinforcement. Measurements of glass transition temperature (T_g) provide a direct insight into the mobility of polymer chains; for the purposes of this study, the T_g was taken as midpoint in the specific heat transition.

The DSC curves for both the systems *i.e.*, DGEBA and TGDDM based hybrid nanocomposites are presented in Figs. 5(a) and 5(b), respectively. All the DSC thermograms displayed single T_g values in the experimental temperature range from 30°C to 250°C. It is observed that the DDS cured DGEBA and TGDDM epoxy systems displayed T_g values at 199°C and 255°C, respectively. When compared with the values of T_g for the DDS-DGEBA epoxy system, the T_g was enhanced with increased loading of OAPS up to 3 wt% into the DDS-DGEBA network. This enhancement could be ascribed to the nanoreinforcement effect of POSS on the polymer matrix. POSS cages on the segmental level could restrict the motion of macromolecular chains, and thus $T_{\rm g}$ is enhanced. While increasing concentration of OAPS into DGEBA epoxy system led to a reduction in the T_g for the hybrid nanocomposites; a finding also reported in several POSS-containing epoxy nanocomposites [26-28]. The depression in the T_g of the nanocomposites at higher loadings of POSS may be attributed by the following factors: (i) incomplete curing reaction of epoxy-amine and (ii) the volume fraction of POSS in the epoxy resin. In the present composite systems, the FT-IR results revealed that the curing reactions in the hybrids also apparently went to completion and that in the POSS-containing hybrids, the POSS cages were bonded covalently within the epoxy matrices. Therefore, the first factor (incomplete curing reactions resulting from the incorporation of POSS cages in the hybrids) can not be the reason for the depression of T_g in the present cases. At higher POSS contents in the hybrids, the volume fraction of POSS in the resin is substantial. In other words, the presence of bulky POSS cages could act as an internal plasticizer, thus giving rise to reduced T_g values in the hybrid systems (> 3 wt% of OAPS). A similar trend was observed in the effect of POSS on the T_g in the TGDDM based epoxy nanocomposites: higher T_g values were obtained

in the TGDDM epoxy systems than the corresponding DGEBA epoxy systems due to the higher epoxy functionality in TGDDM which, in turn, imparts higher crosslink density as expected [29].

3.4 Dynamic mechanical properties

Dynamic mechanical analysis (DMA) was performed on the neat epoxy systems and their hybrids containing 1, 3, 5, 10, and 20 wt% of OAPS as functions of temperature. The tan δ peaks of neat and nanocomposite systems displayed a welldefined relaxation peak in the temperature range of 30 to 350°C as shown in Figs. 6(a) and 6(b), which represents the glass-rubber transition of the polymer. The tan δ spectrum of DDS cured DGEBA and TGDDM epoxy systems exhibited single atransition peaks centered at 201 °C and 260 °C respectively. The tan δ peak of the hybrids containing a small amount ($\leq 3 \text{ wt\%}$) of POSS obviously shifts to a higher temperature while the peaks were markably broader than those of the corresponding neat epoxy systems. The intensity of tan δ at T_g is a measure of the energy-damping characteristics of a material and the breath of the tan δ peak indicates the cooperative nature of the relaxation process of the polymer chains. The concept of cooperativity is related to the ease with which polymer chains move at T_g . If the molecular chains in a polymer resist movement at T_g , then the tan δ peak will be broad. The effect of enhancement of Tg and high cross-linking by the introduction of small amount of POSS cages in to both the DGEBA and TGDDM epoxy systems suggest that the epoxy matrices could be reinforced on the nanoscale level by the POSS cages which were covalently bonded to the epoxy networks. The increasing concentration of POSS (> 3 wt%) in the hybrid epoxy systems, the nanocomposites exhibited lower $T_{\rm g}$ s than

those of the neat epoxy systems due to the decrease in the crosslink densities of the resulting hybrid materials. The decreased densities could be ascribed to the increase in the porosity of the nanocomposites [30]. The porosity of POSS-containing nanocomposites is composed of two portions: one portion comes from an external porosity as a result of the inclusion of bulky POSS, which can be interpreted as the increase in free volume of the nanocomposites caused by the interactions between POSS cages and polymer segments [31]. The second portion of porosity can be attributed to the nanoporosity of the POSS core with a diameter of 0.53 nm. The decreasing crosslink density per unit volume in the hybrid systems leads to a decrease in the value of T_g at higher loading of POSS moleties into the epoxy-amine networks. These results are in a good agreement with those obtained from DSC measurements.

Dynamic storage modulus shown in Figs. 7(a) and 7(b) are the plots of storage modulus as function of temperatures for the neat epoxy and the nanocomposite systems with the OAPS content upto 20 wt%. It is interesting to note that the dynamic storage moduli of all the POSS containing hybrids were significantly higher than those of neat epoxy systems in the glassy state (T < T_g). The improvement in the dynamic storage moduli of POSS containing hybrids could be attributed to the nanoscale dispersion of POSS cages in the hybrid epoxy nanocomposites. The presence of the nanoscale dispersion of POSS in the epoxy matrices could be evidenced by the changes in glass transition temperature as well as tan δ peak width. It is worth noting that for the POSS/epoxy nanocomposites it is seen that all the nanocomposites were close to, or significantly higher than, the control epoxy systems in the rubbery state (T > T_g) of storage moduli. In a crosslinked structure, a rubbery state modulus correlates directly with the network crosslink density. Therefore, the

increasing concentration of POSS (> 3 wt%) in the hybrid systems, the nanocomposites are expected to be lower than that of the control epoxy systems since the massive and bulky POSS cages will reduce the crosslink density of the networks which was evidenced by tan δ peaks. However, it is seen that the storage moduli of the nanocomposites containing POSS are significantly higher than that of the control epoxy systems, implying the significant nanoreinforcement of POSS cages which could be the dominant factor to affect the moduli of the nanocomposites in the present case.

3.5 Thermal Stability

Thermogravimetric analysis was carried out to evaluate the thermal stability of the POSS-containing epoxy nanocomposites and Figs. 8(a) and 8(b) depict the TGA curves of the neat epoxy systems, OAPS, and the POSS-containing epoxy nanocomposites in the temperature range from 30 °C to 900 °C. Within the experimental temperature range, all the TGA curves displayed similar degradation profiles. This observation indicates that the existence of POSS did not significantly alter the degradation mechanism of the matrix polymers. For the pure OAPS, the initial decomposition temperature that was defined as 5% mass loss temperature is 185 °C and the char yield is 38%. For the neat DGEBA epoxy system, the initial decomposition occurred at 371 °C and no residual of decomposition (at 750 °C) was obtained. The initial (5%) decompositions of the nanocomposites are intermediate between those of the neat epoxy systems and OAPS. In addition, the incorporation of OAPS into epoxy networks resulted in a significant effect in improving the thermal stability, resulting in a retarded weight loss rate and an enhanced char yield in the higher temperature region. This effect was increasingly pronounced with increasing the concentration of OAPS in the hybrid systems. This improvement in weight retention was attributed to the POSS constituent, which was combined with the crosslinked network *via* the formation of covalent bonds. Furthermore, the nano-scale dispersion of POSS cages in epoxy matrices is an important factor to contribute the enhanced thermal stability. The similar results were also observed in our previous work on the completely exfoliated clay-epoxy nanocomposites [32].

From Fig. 8(b), it is noted that the initial decomposition occurred at 404 °C and no residual of decomposition at 750 °C was obtained for the DDS cured TGDDM epoxy system as expected. Although a similar trend was maintained in the TGDDM hybrid systems as was observed in the case of DGEBA hybrid systems, TGDDM based epoxy nanocomposites are typically more thermally stable than the DGEBA hybrid systems due to the formation of highly crosslinked networks in the former. Both the DGEBA and TGDDM hybrid nanocomposites exhibited very high char yields, implying that fewer volatiles were released from the nanocomposites during heating. The decreased rate of volatile released from the hybrid materials suggested the improved flame retardance of the materials.

3.6 Dielectric and Water absorption behaviour

The dielectric constant (ϵ ') and dielectric loss (ϵ '') of the DDS cured DGEBA and TGDDM epoxy systems and their hybrid nanocomposites were measured by using impedance analyzer at 30 °C at a frequency of 1 MHz. As shown in Fig. 9, the incorporation of nanoporous POSS molecules into the epoxy nanocomposites resulted in a lower dielectric constant as well as a lower dielectric loss than those of the neat epoxy systems and the reduction of dielectric properties is increased with increasing concentration of OAPS in the hybrid systems. Compared with dielectric constant of the DDS cured DGEBA system (3.56 at 1MHz), the dielectric constant decreased to 2.87 and 2.52 for the nanocomposites having 10 wt% and 20 wt% of OAPS, respectively. The decreasing trend of dielectric properties as the increase of POSS loadings in the hybrids suggest that the increasing of POSS loading decreases the dipole-dipole interactions in the nanocomposites. A few possible interpretations are put forward to account for the reduction in electric dipole interactions in the nanocomposites in line with the increase in POSS loading. It is most likely that the POSS molecule has got inherent porosity, in addition when it is incorporated into epoxy system it also imparts external porosity due to the development of voids in the hybrid systems. This could be inferred from the DSC and DMA results of the nanocomposites which contain higher loadings of POSS (< 3 wt%). A second cause is that the thermally stable inorganic silica core of POSS molecules are simply less polar than the polymer segments, which in turn reduces the dielectric constant and dielectric loss of the epoxy nanocomposites [32]. In particular, the small amount of POSS (≤ 3 wt%) loading in the hybrid systems illustrates the low dielectric constant and low dielectric loss as shown in Table 1 even attaining higher crosslink densities than those of the neat epoxy systems. In this case, the presence of inorganic silica core and thus by the formation of voids in the hybrid systems could be the dominant factor in the hybrid systems. It is well known that the signal propagation delay time of integrated circuits is proportional to the square root of dielectric constant of the matrix, while the signal propagation loss is proportional to the square root of the dielectric constant and dielectric loss of the matrix. Thus, a material with low dielectric constant and low

dielectric loss increases the speed of signal transmission between chips in the packaging.

Apart from structure-related arguments, the polarity of domains is also thought to play a significant role in water absorption. This is because water carries a strong dipole which can easily bind to polar groups. The greater affinity of crosslinked domains for water was frequently invoked, and explained by the presence of strongly polar hydroxyl (-OH) groups. Following Wright's pioneering work, it is well known that epoxy resins typically lose 20K of dry T_g for every 1% of absorbed moisture. These are the reasons for studying the water absorption behaviour in the nanocomposites, which was carried out by immersing the samples completely in deionized water for the period of 7 days at 30 °C. It is worth noting that the POSS reinforced epoxy nanocomposites absorbed less water than the neat epoxy systems (Table 1). The experiments showed very little volume change without any clustering or micro-voiding. The addition of the inorganic content of POSS into the epoxyamine networks reduced the polarity of the polymer since the water uptake is mainly related to the polarity of the polymers and hence to the amount of bound water, rather than the free water trapped in micro-voids of free volume in the nanocomposites.

3.7 X-ray diffraction analysis

Figs. 10(a) and 10(b) display the X-ray diffraction patterns for the pure OPS, pure ONPS, pure OAPS and OAPS containing epoxy nanocomposites. The OPS monomer profile shows many diffraction peaks. There are five distinct diffraction peaks at $2\theta = 8.3^{\circ}$, 11.3°, 19.1° and 25.9° by OPS, corresponding to *d*-spacings at 1.06,

0.78, 0.46 and 0.34 nm, respectively. The pattern is almost identical to the previously reported observation on cyclopentyl methacrylate POSS (cyclopentyl MA-POSS) [33]. The peak corresponding to a *d*-spacing of 1.05 nm reflects the size of POSS molecules and the remaining peaks are due to the rhombohedral crystal structure of POSS molecules. In the case of ONPS, a couple of peaks were observed at $2\theta = 8.3^{\circ}$, 9.2°, corresponding to d-spacings at 1.06 and 0.96 nm, respectively, which indicated the formation of isomers. The peaks appeared at $2\theta = 15^{\circ} - 35^{\circ}$ in OPS were markedly decreased in ONPS which revealed that the formed isomers significantly disrupt the cubic silsesquioxane crystal structure. In the case of OAPS, a small peak was observed at $2\theta = 8^{\circ}$ and it corresponds to 1.10 nm; a very broad amorphous halo was also observed at about $2\theta = 21.4^{\circ}$ (0.42 nm). The *meta* and *para* isomers of OAPS completely disrupt the cubic silsesquioxane crystal structure and result in an amorphous structure. The first peak (Fig. 10(b)) could be explained by some longrange order which is attributed to the inter-silsesquioxane cube distance and the broad halo may be associated with Si-O-Si linkages. For the POSS containing epoxy nanocomposites, the lowered intensity amorphous peak (first peak) represents intersilsesquioxane cube distance, shifts from $2\theta = 8^{\circ}$ (OAPS) to a lower angle $2\theta = 7.6^{\circ}$ in the presence of curing agent. It is believed that the crosslinking reaction with the curing agent generated the longer distance (from 1.10 nm to 1.16 nm) between the POSS cubes. A weak amorphous peak at $2\theta=21.4^{\circ}$ in the diffraction pattern of OAPS is very close to the amorphous peak at 19.5° of the DDS cured epoxy systems, but the intensity in this region does not change as the OAPS increases in the hybrid systems. The amorphous peak at 19.5° in all the DDS cured epoxy nanocomposites is a contribution from control epoxy systems. This implies that OAPS is dispersed into the epoxy network as unassociated and compatible POSS units.

The morphology of the DDS cured DGEBA and TGDDM based systems and their OAPS-containing hybrids was further investigated by SEM. Figs. 11A-11F Show the SEM micrographs of the fractured surfaces of the hybrids frozen under cryogenic condition using liquid nitrogen. After etching with THF, the OAPScontaining system exhibited a featureless morphology and no discernible phase separation was observed (Figs. 11C- 11F). The homogeneous and transparent natures of the mixtures of POSS with epoxy resin indicates that the two components are miscible and this may be ascribed to the formation of covalent bonds between the POSS and the epoxy resin. The amine functionality in the silsesquioxane cages plays a significant role in the formation of these covalent bonds and thus the homogenous morphology. By controlling the type and reactivity of the functional groups in the POSS cages, epoxy nanocomposites with varying morphologies and thermal stabilities can be obtained [23]. The utilization of the reactive POSS (*i.e.* OAPS) resulted in the formation of homogeneous epoxy/POSS nanocomposites. The homogeneous morphology of OAPS/DGEBA epoxy systems was further evidenced by visual observation study (Fig. 12) which clearly indicates that the transparency of the materials could be obtained by tuning the tether structure of POSS molecules.

4. Conclusions

An amino-functionalized POSS derivative (OAPS) was synthesized from phenyl trichlorosilane in three steps and the formation of the octa-amino functionalized POSS structure was conformed by means of FTIR and NMR spectroscopy, and XRD analysis. OAPS was employed to prepare the nanocomposites with DGEBA and TGDDM epoxy resin and DDS was used as a curing agent. The thermosetting DDS cured epoxy nanocomposites containing POSS (at loadings up to 20 wt%) were obtained via in situ polymerization of DGEBA/TGDDM and DDS in the presence of OAPS. When compared with control epoxy systems, the increase in T_{g} at lower POSS loadings ($\leq 3 \text{ wt\%}$) and the decrease in T_g at higher POSS loadings (> 3 wt%) were identified by means of DSC and DMA analysis. In this case, the increase of free volume in the hybrid systems by the effect of bulky POSS cages could be the reason for the depression of T_g in the resulting epoxy nanocomposites. The TGA results showed that the OAPS containing epoxy nanocomposites displayed more pronounced improvements in thermal stability and in char yield than the control epoxy systems. The increasing incorporation of POSS into the epoxy-amine network gives rise to reductions in dipole-dipole interaction and thus reduced water permeability and dielectric constant in the resulting hybrids. The increased rubbery plateau modulus with increasing concentration of POSS (up to 20 wt%) indicates the nanoreinforcement effect of OAPS with the epoxy resins. X-ray diffraction profiles reveal that POSS is dispersed on a nanoscale level into the epoxy network. SEM indicates that the nanometre-scaled homogeneous dispersion of POSS molecules in the epoxy hybrids which could be ascribed the formation of covalent bond between POSS cages and epoxy-amine networks.

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DDS cured Epoxy/POSS Network structure

Scheme 2 Schematic representation of POSS reinforced epoxy nanocomposites

		т	TGA		Dielectric	Dioloctrio	Water
Epoxy type	OAPS wt%	1 _g from DMA	Initial degradation	Char yield at	constant	loss (ε'')	uptake wt%
		°C	(5 wt% loss) °C	750 °C wt%	(1 MHz)	(1 MHz)	
DGEBA	0	201	371	0	3.56	0.174	1.50
DGEBA	1	207	360	5	3.39	0.161	1.47
DGEBA	3	214	355	12	3.25	0.135	1.45
DGEBA	5	188	346	21	3.01	0.121	1.41
DGEBA	10	183	344	27	2.87	0.103	1.36
DGEBA	20	177	341	30	2.52	0.072	1.30
TGDDM	0	260	403	06	4.81	0.318	2.31
TGDDM	1	271	387	19	4.62	0.295	2.26
TGDDM	3	279	376	31	4.45	0.277	2.21
TGDDM	5	245	369	32	4.21	0.223	2.16
TGDDM	10	241	360	39	3.98	0.202	2.12
TGDDM	20	237	353	42	3.64	0.169	2.08

Table 1. Thermal and Dielectric properties of OAPS reinforced DDS-epoxy nanocomposites

Figure captions

Scheme 1 Synthesis of octaaminophenylsilsesquioxane

Scheme 2 Schematic representation of POSS reinforced epoxy

Nanocomposites

- 1. Fig. 1 (a). FT-IR spectrum of OPS
- 2. Fig. 1(b). Solid ²⁹Si NMR of OPS
- 3. Fig. 2(a). FT-IR spectrum of ONPS
- 4. Fig. 2(b). ¹H NMR spectrum of ONPS
- 5. Fig. 2(c) ¹³C NMR spectrum of ONPS
- 6. Fig. 2(d) ²⁹Si NMR spectrum of ONPS
- 7. Fig. 2(d) ²⁹Si NMR spectrum of ONPS
- 8. Fig. 3(a) FT-IR spectrum of OAPS
- 9. Fig. 3(b). ¹H NMR spectrum of OAPS
- 10. Fig. 3(c). ¹³C NMR spectrum of OAPS
- 11. Fig. 3(d). ²⁹Si NMR spectrum of OAPS

- 12. Fig. 4. FT-IR spectrum of OAPS reinforced epoxy nanocomposites (a) OAPS reinforced DDS-DGEBA epoxy nanocomposites and (b) OAPS reinforced DDS-TGDDM epoxy nanocomposites
- 13. Fig. 5. DSC thermogram of OAPS reinforced epoxy nanocomposites (a)OAPS reinforced DDS-DGEBA epoxy nanocomposites and (b) OAPSreinforced DDS-TGDDM epoxy nanocomposites.
- 14. Fig. 6. Tan δ vs Temperature of OAPS reinforced epoxy nanocomposites (a) OAPS reinforced DDS-DGEBA epoxy nanocomposites and (b) OAPS reinforced DDS-TGDDM epoxy nanocomposites
- 15. Fig. 7. Storage modulus vs Temperature of OAPS reinforced epoxy nanocomposites (a) OAPS reinforced DDS-DGEBA epoxy nanocomposites and (b) OAPS reinforced DDS-TGDDM epoxy nanocomposites
- 16. Fig. 8. TGA of OAPS reinforced epoxy nanocomposites (a) OAPS reinforced DDS-DGEBA epoxy nanocomposites and (b) OAPS reinforced DDS-TGDDM epoxy nanocomposites
- 17. Fig. 9. Dielectric constant (ε') and dielectric loss (ε'') of OAPS-epoxy nanocomposites
- 18. Fig. 10(a). XRD patterns for OPS, ONPS and OAPS

- 19. Fig. 10(b). XRD patterns for DDS-DGEBA, DDS-TGDDM and their POSS nanocomposites
- 20. Fig. 11. SEM morphology of OAPS-epoxy/DDS nanocomposites A) neat DGEBA, B) neat TGDDM, C) 1 wt% of OAPS in DGEBA, D) 1 wt% of OAPS in TGDDM, E) 20 wt% of OAPS in DGEBA and F) 20 wt% of OAPS in TGDDM
- 21. Fig. 12. Visual observations of A) 3 wt% OAPS-DGEBA/DDS nanocomposites and B) 3 wt% ONPS-DGEBA/DDS nanocomposites



(a)



(b)

Fig. 4. FT-IR spectrum of OAPS reinforced epoxy nanocomposites (a) OAPS reinforced DDS-DGEBA epoxy nanocomposites and (b) OAPS reinforced DDS-TGDDM epoxy nanocomposites



(a)



(b)

Fig. 5. DSC thermogram of OAPS reinforced epoxy nanocomposites (a) OAPS reinforced DDS-DGEBA epoxy nanocomposites and (b) OAPS reinforced DDS-TGDDM epoxy nanocomposites.



(a)



(b)

Fig. 6. Tan δ vs. Temperature of OAPS reinforced epoxy nanocomposites (a) OAPS reinforced DDS-DGEBA epoxy nanocomposites and (b) OAPS reinforced DDS-TGDDM epoxy nanocomposites





Fig. 7. Storage modulus *vs.* Temperature of OAPS reinforced epoxy nanocomposites (a) OAPS reinforced DDS-DGEBA epoxy nanocomposites and (b) OAPS reinforced DDS-TGDDM epoxy nanocomposites





Fig. 8. TGA of OAPS reinforced epoxy nanocomposites (a) OAPS reinforced DDS-DGEBA epoxy nanocomposites and (b) OAPS reinforced DDS-TGDDM epoxy nanocomposites



Fig. 9. Dielectric constant (ϵ ') and dielectric loss (ϵ '') of OAPS-epoxy nanocomposites



Fig. 10(a). XRD patterns for OPS, ONPS and OAPS



Fig. 10(b). XRD patterns for DDS-DGEBA, DDS-TGDDM and their POSS nanocomposites



Fig. 11. SEM micrographs of OAPS-epoxy/DDS nanocomposites A) neat DGEBA,
B) neat TGDDM, C) 1 wt% of OAPS in DGEBA, D) 1 wt% of OAPS in TGDDM, E) 20 wt% of OAPS in DGEBA and F) 20 wt% of OAPS in TGDDM



Fig. 12. Visual observations of A) 3 wt% OAPS-DGEBA/DDS nanocomposites and B) 3 wt% ONPS-DGEBA/DDS nanocomposites