Synthesis and Characterization of a POSS-Maleimide Precursor for Hybrid Nanocomposites

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ABSTRACT

Epoxy-POSS based hybrid nanocomposites are prepared by *in situ* polymerization of a homogeneous blend of the diglycidylether of bisphenol-A (DGEBA) and 4,4'-diaminodiphenylmethane (DDM) in the presence of octa(maleimidophenyl)silsesquioxane (OMPS). The reaction of a maleimido-functionalised POSS cube with the epoxy resin is studied by Fourier transform infrared (FTIR) analysis and the formation of nanocomposites is confirmed by wide-angle X-ray diffraction (WAXD) and scanning electron microscopy (SEM). Dynamic mechanical analysis (DMA) studies indicate that the crosslinking structures of the nanocomposite networks are predominantly formed

between the terminal maleimide double bonds and the amino groups of DDM through a Michael addition reaction to form an aspartimide. The values of the glass transition temperatures (T_g) decrease with increasing POSS-maleimide content and this is likely to be due to the inclusion of POSS cages into the system and consequent increase in free volume. The dynamic thermal stability of the cured polymers is increased by increasing the POSS content in the hybrid epoxy matrices as evidenced from thermogravimetric analysis (TGA) data.

Keywords: epoxy resin, octamaleimidophenyl silsesquioxane, hybrid nanocomposites.

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1. INTRODUCTION

Scientists who are currently involved in modern, interdisciplinary materials research, which cuts across traditional boundaries, are now intensely interested in the development of nanomaterials for a wide variety of reasons, but principally because these materials offer exciting new challenges and opportunities in the different branches of science and technology. It is now widely recognized that reductions in the size of component particles influence the interfacial interactions between them and this can, in turn, enhance the material properties to an appreciable extent [1]. Consequently, it is also possible to develop materials that are **completely discontinuous *i.e.* contain both organic and inorganic phases** and such materials exhibit nonlinear changes in properties with respect to macroscopic composites that are made of the same component phases. In the case of nanocomposites, the interfacial interactions dominate global properties and thus can offer properties not anticipated by knowledge of bulk phase properties [2].

The development of nanomaterials comprising organic and inorganic skeletons will provide a new class of nanocomposites with a variety of improved properties. In this context, hybridizing POSS derivatives with industrially valuable polymeric components can lead to new chemical feed stock technology for the development of interphased nano-hybrid materials. There is already evidence to support the belief that modification of polymeric materials using derivatives of polyhedral oligomeric silsesquioxane (POSS) is expected to upgrade many of their useful properties namely thermal stability [3], oxidation resistance [4], resistance to atomic oxygen in low earth orbit [5,6] glass transition temperature [7], tensile strength [8], fracture toughness [9], abrasion resistance,

dimensional stability, dielectric behaviour, optical properties and weather resistance [10-12].

POSS modification of polymers has also been shown to improve processing and provide better service performance under adverse environmental conditions. Consequently, the development of hybrid nanocomposites with well defined structures is one of the most efficient concepts towards designing nanohybrid materials [13-15] in combination with commodity and/or engineering polymers with improved performance for advanced applications.

In the present work, polymeric nanocomposite materials, suitable for advanced industrial and aerospace applications, and based on a novel POSS-maleimide (OMPS) and an epoxy resin have been developed and characterized. The hybrid nanocomposites are shown to offer improved thermal and mechanical properties over analogous polymer composite materials.

2. EXPERIMENTAL

2.1 Materials

The epoxy resin used in the work is based on the diglycidyl ether of bisphenol-A (DGEBA) and is commercially available from Ciba-Geigy as LY 556 (epoxy equivalent = 180-190 eq/kg, viscosity 10,000 cP). The curing agent used is diaminodiphenylmethane (DDM) (HT972, Ciba-Geigy, amine equivalent = 49.5 eq/kg). Phenyltrichlorosilane (40%), methanolic benzyltrimethylammonium hydroxide (10 wt% Pd/C), and maleic anhydride were purchased from Lancaster Chemicals UK. Other solvents were procured from SRL in India. Tetrahydrofuran (THF) was used after

purification by distilling it in presence of sodium metal; all other chemicals were used without further purification.

2.2 Characterization methods

FTIR spectra of the samples were obtained using a Perkin Elmer (Model RX1) spectrometer (cured samples were ground with solid KBr). ^1H (500 MHz), ^{13}C (200 MHz), and ^{29}Si (79.43 MHz) nuclear magnetic resonance (NMR) spectra were recorded on a Jeol GSX 400 spectrometer operating at 298 K with tetramethylsilane (TMS) as an internal standard; solutions were prepared in THF. Gel permeation chromatography (GPC) was performed using a Waters 2690 separation module and a Waters 410 differential refractometer detector; calibration was performed using a series of polystyrene standards of narrow polydispersity. Differential scanning calorimetry was performed using both Netzsch and TA instruments calorimeters (sample sizes 5-10 mg, ramp rate 10 K/min., sealed aluminium pans, nitrogen atmosphere). Dynamic mechanical analysis was undertaken using a Netzsch 242 DMA at a heating rate of 10 K/min. from 30 to 200°C (frequency 1 Hz, 3 point bending cantilever, sample dimensions 55 x 10 x 3 mm³). Thermogravimetric (TG) analysis was performed using a TA Instruments TA2000 analyzer. Cured samples were analyzed in open (silicon) pans at 20 K/min. in a N₂ atmosphere up to a maximum temperature of 1000°C. Wide-angle X-ray spectra were obtained using a Rich Seifert (Model 3000) diffractometer (with Cu K α radiation ($\lambda = 0.15418$ nm) for the ground powder of cured composites. The spectral window ranged from $2\theta = 2^\circ$ to $2\theta = 20^\circ$. Scanning electron microscopy of fracture surfaces was performed using a JEOL JSM Model 6360 microscope. The fractured

surfaces of the specimens were coated with platinum and were exposed to accelerating voltage 20 kV.

2.3 Synthesis of Octaphenyl Silsesquioxane (OPS)

Phenyltrichlorosilane (132.25 g, 100 mL, 0.625 mol.) was placed, along with benzene (630 mL), in a 3-L, three-necked, round-bottom flask fitted with a magnetic stirrer and a dropping funnel. Water (330 g) was added dropwise, and the reaction was carried out at 25°C with constant agitation for 12 hours, the reaction mixture was washed with water until it became neutral, and the aqueous layer was removed. To the organic layer was added methanolic benzyl trimethylammoniumhydroxide (40%, 17 mL) and the resulting mixture was refluxed for 4 hours. The reaction mixture was allowed to stand at 25°C for 4 days and was further refluxed for 24 hours. A white, solid powder weighing 79 g (yield 97.8%) was obtained by filtration, and the product (octaphenyl silsesquioxane) was recrystallized using 1,2-dichlorobenzene [16].

2.4 Synthesis of Octa (nitrophenyl) Silsesquioxane (ONPS)

ONPS was synthesized by adopting a procedure previously reported elsewhere [17]. Fuming nitric acid (360 mL) was placed in a three-necked, round-bottom flask, equipped with a mechanical stirrer, and the flask was cooled in an ice bath before OPS (60 g) was added portion-wise. The resulting mixture was kept in an ice cold condition for an hour with constant agitation for 12 hours at 25°C. Then the reaction mixture was poured on to an ice and a light yellow precipitate obtained was removed by filtration,

washed with deionized water until neutral pH was obtained, and then washed twice with ethanol (2 x 120 mL). The solid product obtained (octanitrophenyl silsesquioxane) was air-dried at 25°C for 12 hours and weighed. (72g yield 89.2%).

2.5 Synthesis of Octa (aminophenyl) SilSesquioxane (OAPS)

Laine's method [2] was followed to synthesize OAPS, wherein ONPS (10 g, 7.18 mmol.) and 10 wt% Pd/C (0.61g 0.578mmol.) were placed in a three-necked, round-bottom flask fitted with a magnetic stirrer under a nitrogen atmosphere. Freshly distilled THF (80 mL) and triethylamine (80 mL) were then added to the vessel and the resulting mixture was heated to 60°C, followed by the gradual addition of 85% formic acid (10.4 mL, 0.23 mol.). The latter resulted in the evolution of CO₂, before the solution separated into two layers was allowed to stand at 60°C for 12 hours. The THF layer was separated followed by the addition of a mixture of THF (50 mL) and water (50 mL) to the black residue and both the THF layers were combined and filtered through celite. Ethylacetate (50 mL) was added to the filtrate, which was washed with water and dried over anhydrous magnesium sulphate, and precipitated with hexane (2 L). The resulting fine white precipitate (octaminophenyl silsesquioxane) was filtered and dried *in vacuo* at 60°C for 2 weeks.

2.6 Synthesis of Octa(maleimidophenyl) Silsesquioxane (OMPS)

In a 100 mL flask fitted with a magnetic stirrer, OAPS (1.5g, 1.3 mmol.) was dissolved in *N,N*-dimethyl acetamide (25 mL). Maleic anhydride (10.2 g, 10.4 mmol.)

was added slowly portion-wise and the resulting reaction mixture was stirred for 1 hour at 25°C under nitrogen atmosphere. The resulting maleamic acid was imidized chemically by adding triethylamine (0.21 mL) followed by acetic anhydride (2.5 mL), dropwise and the mixture refluxed at 60 °C for 2 hours. The product was extracted with ethyl acetate (90 mL) followed by washing with water. The organic layer was dried over sodium sulphate and precipitated using hexane (500 mL) before the resulting solid product was filtered and dried *in vacuo* at 25°C. The spectral and molecular weight data for OPS, ONPS, OAPS and OMPS are presented in Table 1.

2.7 Hybrid Nanocomposites

The hybrid POSS nanocomposites used in this study were developed by thoroughly mixing a fixed amount of epoxy resin (DGEBA) and varying amounts (5, 10, and 15 wt %) of octamaleimido-POSS at 95-100°C for 10 minutes with constant agitation followed by curing with a stoichiometric amount (with respect to epoxy) of diaminodiphenylmethane (DDM). The resulting homogenous hybrid blend was degassed to remove entrapped air and poured into a preheated mould, maintained at 120°C for 2 hours, post cured at 180°C for 4 hours and characterized.

3. RESULTS AND DISCUSSION

3.1 Molecular structure

The FTIR spectrum of OMPS (Figure 1) shows the complete disappearance of the N-H stretching band of the primary amine at 3360 cm⁻¹ and the appearance of bands at

3100 cm^{-1} , corresponding to the H-C= vibration, 1610 cm^{-1} representing the conjugated C=C stretch of the imide ring, and 1710 cm^{-1} representing the conjugated C=O stretch of the imide ring. The ^1H NMR spectra for ONPS, OAPS and OMPS are shown in Figure 2. For ONPS, the chemical shifts corresponding to the aromatic protons is in the range 7.0-9.0 ppm; those for the aromatic protons of OAPS lie in the range of 6.5-7.5 ppm and for amino protons in the range of 4.0-5.0 ppm, which are in the ratio of 2:1 and are in good agreement with the results of Laine *et al.* [2]. The disappearance of signals corresponding to the amino protons in the ^1H NMR spectrum of OMPS confirms the complete conversion of amine to maleimide group (Figure 2). The ^{29}Si NMR spectra of ONPS, OAPS and OMPS are presented in Figure 3: for ONPS the appearance of two shifts at -79 ppm and -82 ppm, indicates the presence of two isomers containing *meta*- and *para*-disubstituted species. Data obtained from GPC analysis (Table 1) indicate that OPS, ONPS, OAPS, and OMPS have low polydispersity indices (PDIs) (*i.e.* narrow molecular weight distributions), which indicate that the POSS core has remained intact during the chemical conversions.

3.2 Spectral Analysis and Cure Behaviour

The FTIR spectral bands for OPS, ONPS, OAPS and OMPS are presented in Table 1: the band at 3096 cm^{-1} is due to the H-C= stretching vibration and is widely accepted as a reference [18] to follow the conversion of POSS-maleimide double bonds. The spectra for blends of the epoxy and POSS-maleimide (OMPS) of varying compositions are presented in Figure 4. From these data, it can be seen that the disappearance of peak at 916 cm^{-1} (attributed to epoxy ring breathing) indicates the

curing reaction of epoxy, and the appearance of peak at 1113 cm^{-1} (Si-O-Si asymmetric stretch) confirms the existence of POSS cube structure. The disappearance of the band at 3100 cm^{-1} also confirms that H-C= stretching of POSS-maleimide is consumed by the Michael addition reaction, since the homopolymerization reaction of OMPS requires higher temperatures than that required for curing the epoxy/DDM system. In Figure 1, showing the IR spectra of OMPS, DDM and OMPS/DDM systems, the disappearance of the peak at 3100 cm^{-1} , corresponding to the maleimide double bond in OMPS, confirms the existence of the Michael addition reaction with the amino group of DDM and the formation of an aspartimide [19]. A previous kinetic study of the thermal polymerization of aryl *bis*-maleimides and *bis*-citraconimides confirms that the Michael addition reaction occurs through an ionic mechanism, which proceeds much more quickly than the BMI homopolymerization [20-25].

The FTIR studies confirm that the formation of hybrid POSS-maleimide modified epoxy system proceeds through the following routes: (i) the reaction between amino groups of DDM and the oxirane ring of the epoxy resin (Scheme 2a) and (ii) the reaction between the amino groups of DDM and the maleimide double bonds through Michael addition (Scheme 2c). The curing reaction between the epoxy and DDM commences at 120°C and reaches its peak maximum temperature at 164°C (Figure 5). The large exotherm obtained during the cure reaction of epoxy-DDM may be attributed to a combination of (i) the oxirane ring-opening reaction with active amino hydrogens of DDM and (ii) the autocatalytic reaction of the oxirane ring with pendent hydroxyl groups of epoxy resin and hydroxyl groups formed during cure reactions [28] (Scheme 2b).

The single value of glass transition temperature (T_g) obtained for the hybrid OMPS-epoxy cured with DDM indicates that the hybrid materials developed in the present work represent a single chemical entity. Furthermore, these hybrids display a unimodal exotherm which may be due to smaller quantities of OMPS incorporation when compared with epoxy as evidenced from DSC cure exotherm (Figure 5). The single cure exotherm peak (unimodal cure exotherm) obtained for all the OMPS modified epoxy-DDM hybrids indicates that the latter are formed by *in situ* polymerization with complete homogeneity as evidenced from DSC cure exotherm (Figure 5). Data obtained from wide-angle X-ray diffraction (WAXD) studies and scanning electron microscopy confirm the homogeneous dispersion of nanosized POSS molecules within the epoxy matrices.

3.3 Thermal and Thermomechanical behaviour of nanocomposites

3.3.1 Thermal properties (Differential Scanning Calorimetry)

Differential Scanning thermograms of the hybrid epoxy resins containing unmodified 5, 10 and 15 wt% OMPS are presented in Figure 6: the T_g value obtained for the epoxy/DDM system is 164°C and those for the hybrids incorporating 5, 10 and 15 wt% OMPS modified epoxy-DDM systems are 161°C, 159°C and 156°C respectively. The reduction in the values of T_g for the hybrid systems decreases as the percentage of OMPS increases, when compared with that of unmodified epoxy DDM cured system. This reduction is probably due to the enhancement of free volume imparted by the bulky nature of POSS cages. It is further inferred that the decrease in the value of T_g is due to the co-reaction between the maleimide residue and the amino group of the DDM and occurs most favourably through the Michael addition (Scheme 2c) rather than maleimide

homopolymerization. The Michael addition reaction leads to the formation of thermally relatively weak aspartimide linkages, and ultimately reduces the crosslink density due to chain extension [22], whereas OMPS homopolymerization leads to the formation of a stable C-C linkage (since homopolymerization would be expected to enhance the value of T_g due to the enhancement in crosslink density). Furthermore, the homopolymerization of POSS-maleimide takes place at higher temperatures than the epoxy/DDM cure reaction.

3.3.2 Dynamic Mechanical Analysis (DMA)

In addition to DSC analysis, DMA was employed to measure the stiffness and mechanical damping from the values of loss tangent ($\tan\delta$) and the degree of crosslinking. Thus, DMA curves obtained for both the unmodified epoxy and OMPS-modified epoxy systems (with increasing weight percentages 5, 10 and 15 wt%) are presented as a function of temperature in [Figure 7](#) (storage modulus) and [Figure 8](#) ($\tan\delta$). [Figure 7](#) represents the storage modulus (E') of the unmodified epoxy and those for the hybrids containing 5, 10 and 15 wt% of OMPS modified epoxy hybrids. It is apparent that the E' values of the OMPS modified hybrids are higher than those of the unmodified epoxy systems. The value of E' is higher in the case of 5 wt% OMPS modified system than the 10 and 15 wt% OMPS modified epoxy systems; this may be due to the inclusion of bulky POSS group increasing the free volume of the hybrids. The plots of the corresponding storage moduli ([Figure 7](#)) show that the lower temperature modulus of the epoxy is improved by hybrid formation [27, 29].

Figure 8 shows the loss tangent ($\tan\delta$) values of the unmodified, 5, 10 and 15 wt% OMPS modified epoxy-DDM systems and the values of loss tangent increase with increasing percentage incorporation of OMPS into the epoxy systems. Above T_g the damping behaviour increases as the percentage of OMPS increases which, in turn, results in a decrease in the crosslink density of the hybrids. This is due to the incorporation of OMPS into the epoxy system which enhances the free volume of the hybrid epoxy systems with consequent reduction in the values of T_g [20, 21] as evidenced by the thermal studies (DSC). The crosslink density of the hybrids can be calculated based on the network theory of rubber elasticity [32, 33] and is represented by the equation given below:

$$\rho = \frac{E'}{3d\phi RT}$$

where E' is determined by DMA under the following conditions: frequency, 1, 2, 4, 10 Hz; temperature 40°C; where d is the density, ϕ is the front factor (where $\phi = 1$), R is the gas constant, and T is the absolute temperature.

3.3.3 Thermal stability (Thermogravimetric analysis)

Thermogravimetric analysis of hybrid epoxy systems was carried out up to 1000°C at a heating rate of 20 K/min. in a N_2 atmosphere. Figure 9 shows the TG curves of the cured unmodified epoxy, OMPS, and OMPS-epoxy/DDM nanocomposites containing 5,

10, and 15 wt% OMPS. From the thermogram the unmodified epoxy-DDM undergoes initial degradation at 405°C with the maximum weight loss taking place at 423°C and no residual char left at 754°C. The incorporation of POSS-maleimide into the epoxy resin improves the thermal stability significantly according to the concentration of POSS derivative [23]. From the thermogram the initial degradation temperature for the POSS-epoxy hybrids are significantly lower than that of the unmodified epoxy DDM-cured systems and it is believed that this is due to weak interaction and lower crosslinking of the hybrid systems.

In the case of OMPS, the initial decomposition occurs at *ca.* 120°C, considerably lower than that of unmodified epoxy cured with DDM and a char yield of 46 % was obtained. However, the incorporation of 5, 10 and 15 % POSS cube into the epoxy resin enhances the residual char yield to 24.7 %, 26.3 %, and 28.6 % respectively at 1000°C and this indicates the utility of the hybrid materials where high thermal stability is required.

3.4 Morphological Studies

The wide-angle X-ray diffraction (WAXD) patterns of OMPS and OMPS/epoxy-DDM hybrids systems are presented in **Figure 10**. For OMPS, a high-intensity peak was observed at $2\theta = 5.3^\circ$, corresponding to 1.7 nm and a peak was observed at *ca.* $2\theta = 20^\circ$. No sharp and narrow peaks were observed due to the presence of a *meta* and *para* isomeric mixture of OMPS [30,31]. Further, the peak at 5.3° is absent in the diffraction patterns of the hybrid OMPS/epoxy-DDM cured systems. The intensity of the halo peak at *ca.* $2\theta = 20^\circ$ in the case of hybrid OMPS indicates that OMPS is well dispersed in the epoxy-DDM network in the form of single chemical entity. In addition to WAXD

measurements, scanning electron microscopy (SEM) was employed to investigate the morphology of unmodified epoxy and hybrid OMPS epoxy/DDM systems (Figure 11). The SEM micrograph of the fractured surface of the unmodified epoxy system (Figure 11a) reveals a smooth, glassy, and homogeneous microstructure without any plastic deformation. Similarly, the fractured surfaces of the OMPS modified (5 wt%) epoxy/DDM systems (Figures 11b and 11c) also indicates homogeneous morphology without any apparent phase separation.

4. CONCLUSION

An octafunctionalised POSS maleimide precursor (OMPS) was synthesized using phenyl trichlorosilane and characterised using FTIR, ^1H NMR, ^{29}Si NMR spectroscopy and GPC analysis. OMPS-modified epoxy hybrid nanocomposites were developed by *in situ* polymerization of DGEBA and DDM with varying (5, 10, and 15 wt%) percentages of OMPS; curing behaviour of hybrid materials was confirmed by an FTIR and DSC analysis. Wide-angle X-ray diffraction and scanning electron microscopy ascertain the nanoreinforcement of OMPS in the epoxy/DDM systems. The apparent reduction in the values of T_g is due to the increase in free volume imparted by the bulky POSS cages and the formation of aspartimide through Michael addition reaction, which lowers the crosslink density of the resulting hybrid. The values of T_g obtained from thermomechanical studies (DMA) and DSC analysis are in good agreement. Thermogravimetric analysis suggests that the OMPS-modified epoxy nanocomposites exhibit improved thermal stability when compared with that of unmodified cured epoxy resins. The data obtained from thermomechanical and thermal stability studies indicate that the hybrid OMPS-modified epoxy nanocomposites that it may be possible to use

these materials in the fabrication of advanced composite components for high performance applications.

Acknowledgement

The authors thank the Department of Science and Technology (DST), New Delhi for Financial support. No.SR/S3/ME/040/2002-SERC-Engg. Government of India.

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Table 1 Spectral and Molecular weight characterization data of OPS, ONPS, OAPS and OMPS.

Analysis	OPS	ONPS	OAPS	OMPS
FTIR	$\nu_{\text{Si-O}} = 1117 \text{ cm}^{-1}$, $\nu_{\text{C-H}} = 3074$ and 2923 cm^{-1} , $\nu_{\text{phenyl}} = 1595$ and 1490 cm^{-1} .	$\nu_{\text{Si-O}} = 1159 \text{ cm}^{-1}$, $\nu_{\text{C-H}} = 3089$ and 2863 cm^{-1} , $\nu_{\text{phenyl}} = 1610$ and 1469 cm^{-1} , $\nu_{\text{NO}_2} = 1535$ and 1347 cm^{-1} .	OAPS: $\nu_{\text{Si-O}} = 1125 \text{ cm}^{-1}$, $\nu_{\text{C-H}} = 3037 \text{ cm}^{-1}$, $\nu_{\text{phenyl}} = 1610$ and 1469 cm^{-1} , $\nu_{\text{N-H}} = 3376 \text{ cm}^{-1}$, $\delta_{\text{N-H}} = 1622 \text{ cm}^{-1}$.	$\nu_{\text{Si-O}} = 1128 \text{ cm}^{-1}$, $\nu_{\text{C-H}} = 3103 \text{ cm}^{-1}$, $\nu_{\text{C=O(imide)}} = 1717 \text{ cm}^{-1}$, $\nu_{\text{C-N}} = 1381 \text{ cm}^{-1}$.
NMR		^1H NMR (δ , ppm): 7.8 (d, aromatic protons), 8.0-8.5 (m, aromatic protons), 8.6 (d, aromatic protons). ^{29}Si NMR (δ , ppm): -69, -71.	^1H NMR (δ , ppm): 6.7, 7.0 (b, aromatic protons), 4-5 (b, amine protons).	^1H NMR (δ , ppm): 7.2, 8.0 (b, aromatic protons), 7.1 (b, aromatic protons), ^{13}C NMR (δ , ppm): 170.5 ($>\text{C=O}$), 132.3, 135.4 (aromatic carbons), 129.7 (C=C).
GPC	$M_n = 948$; $M_w = 1008$; PDI = 1.05; FW = 1036.	$M_n = 1255$; $M_w = 1429$; PDI = 1.12; FW = 1394.	$M_n = 2129$; $M_w = 2786$; PDI = 1.3; FW = 1160.	$M_n = 2018$; $M_w = 2386$; PDI = 1.18; FW = 1792.

Scheme 1. Synthesis of POSS – Maleimide Nano Precursor (OMPS).

Scheme 2. Simplified reactions involved during curing.

Figure 1. FTIR spectra of (a) OMPS/DDM, (b) DDM and (c) OMPS.

Figure 2. ^1H NMR spectra of OMPS, OAPS, and ONPS.

Figure 3. ^{29}Si NMR spectra of OMPS, OAPS , and ONPS.

Figure 4

Figure 4. FTIR spectra of (a) OMPS, (b) DGEBA, (c) DGEBA-DDM, (d) DGEBA-DDM – 5 % OMPS, (e) DGEBA- DDM – 10 % OMPS.

Figure 5. DSC thermograms (exo upwards) of OMPS /epoxy – DDM systems during cure: (a) DGEBA-DDM, (b) DGEBA-DDM – 5 % OMPS, (c) DGEBA-DDM – 10 % OMPS, (d) DGEBA-DDM – 15 % OMPS.

Figure 6. DSC thermograms (Exo upwards) of (a) DGEBA-DDM, (b) DGEBA-DDM – 5 % OMPS, (c) DGEBA-DDM – 10 % OMPS, (d) DGEBA-DDM – 15 % OMPS.

Figure 7. DMA analysis showing storage modulus (E') of (a) unmodified, (b) DGEBA-DDM – 5 % OMPS, (c) DGEBA-DDM – 10 % OMPS and (d) DGEBA-DDM-15 % OMPS systems.

Figure 8. DMA analysis showing $\tan \delta$ of (a) unmodified, (b) DGEBA-DDM – 5 % OMPS, (c) DGEBA-DDM – 10 % OMPS and (d) DGEBA-DDM – 15 % OMPS.

Figure 9. TGA of (a) OMPS, (b) DGEBA-DDM, DGEBA-DDM – 5 % OMPS, DGEBA-DDM – 10 % OMPS and DGEBA-DDM – 15 % OMPS.

Figure 10. XRD pattern of (a) octamaleimidophenyl POSS (OMPS) and (b) OMPS/epoxy-DDM cured hybrid system.

Figure 11. SEM micrograms of (a) unmodified epoxy/DDM system, (b) octamaleimidophenyl POSS (OMPS)(5%) modified epoxy/DDM system at 1 μm and (c) octamaleimidophenyl POSS (OMPS) (5%) modified epoxy/DDM system at 50 μm .