Studies of anhydride-cured epoxy networks with bonded and unbonded polyhedral oligomeric silsesquioxane (POSS)

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STUDIES OF ANHYDRIDE-CURED EPOXY NETWORKS
WITH BONDED AND UNBONDED POLYHEDRAL
OLIGOMERIC SILSESQUOXANE (POSS)

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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OLIGOMERIC SILSESQUOXANE (POSS)**

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A

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TABLE OF CONTENTS

ACKNOWLEDGEMENTS

TABLE OF CONTENTS.....	i
LIST OF FIGURES, SCHEMES & TABLES.....	v
LIST OF ABBREVIATIONS & ACRONYMS	xi
ABSTRACT.....	xiii
1 INTRODUCTION	1
1.1 Objectives.....	4
1.2 Organization of thesis	6
2 REVIEW OF LITERATURE & THEORY	7
2.1 Polyhedral Oligomeric Silsesquioxanes (POSS)	7
2.1.1 Structure of POSS	7
2.1.2 POSS chemistry	9
2.1.3 Properties.....	11
2.1.4 POSS/polymer nanocomposites	12
2.2 POSS as intercalating agent in montmorillonite clay	13
2.2.1 Structure of montmorillonite clay	13
2.2.2 POSS surfactants in clay/polymer nanocomposites	15
2.3 Epoxy resins.....	17
2.3.1 Epoxy structure	17
2.3.2 Cure chemistry in epoxy-anhydride system.....	19
2.3.3 Properties and applications of anhydride-cured epoxies.....	22

2.3.4	Cure kinetics of epoxy-anhydride systems	23
2.3.5	Kinetic models	24
2.4	Epoxy Nanocomposites.....	25
2.5	POSS/epoxy nanocomposites	26
2.5.1	POSS as cross-linkers	26
2.5.2	Pendent POSS as a reinforcing agent.....	32
2.5.3	Unbonded POSS as molecular silica.....	34
2.6	Clay/epoxy Nanocomposites.....	35
2.7	Summary	36
3	INFLUENCE OF CURE KINETICS ON PROPERTIES OF POSS-EPOXY CROSS-LINKED NETWORKS.....	37
3.1	Experimental	38
3.1.1	Materials.....	38
3.1.2	Synthesis of POSS-epoxy cross-linkers	38
3.1.3	Preparation of the hybrid epoxy networks	42
3.1.4	Cure kinetics.....	43
3.1.5	Monitoring of Stage I reaction	44
3.1.6	Synthesis of POSS-anhydride	45
3.1.7	Preparation of POSS-anhydride/epoxy hybrids	46
3.1.8	Characterization	46
3.2	Results and Discussion.....	47
3.2.1	Effect of catalyst concentration.....	47
3.2.2	Cure kinetics.....	50
3.2.3	Effect of pre-mixing.....	52
3.2.4	Effect of post-cure time.....	58

3.2.5 Thermal properties	59
3.2.6 Effect of POSS tether length on cure kinetics.....	62
3.2.7 Anhydride-functionalized POSS hybrids.....	65
3.2.8 Summary	69
4 CATALYTIC AND REINFORCING EFFECTS OF POSS-IMIDAZOLIUM	
SURFACTANTS IN EPOXY AND CLAY/EPOXY SYSTEMS.....	71
4.1 Experimental	72
4.1.1 Materials.....	72
4.1.2 Synthesis of POSS-imidazolium surfactant	72
4.1.3 Modification of MMT clay	73
4.1.4 Preparation of the epoxy hybrid resins.....	74
4.1.5 Cure kinetics.....	75
4.1.6 Characterization	76
4.2 Results and Discussion.....	78
4.2.1 Catalytic effects of POSS-IMC and POSS-MMT.....	78
4.2.2 Morphological studies.....	83
4.2.3 Thermo-mechanical and thermal properties.....	90
4.2.4 Summary	93
5 INTERACTIONS OF UNBONDED POSS ON FILLER DISPERSION AND	
THERMAL PROPERTIES OF EPOXY NETWORKS	94
5.1 Experimental	95
5.1.1 Materials.....	95
5.1.2 Synthesis of the unbonded POSS fillers.....	95
5.1.3 Preparation of POSS-filled epoxy hybrids.....	98
5.1.4 Calculation of solubility parameters	99

5.1.5 Characterization	100
5.2 Results and Discussion.....	102
5.2.1 Solubility of unbonded POSS in epoxy	102
5.2.2 Morphologies of the unbonded POSS hybrids.....	103
5.2.3 Thermal properties	107
5.2.4 Thermal stability	111
5.2.5 Surface properties.....	113
5.2.6 Summary	115
6 CONCLUSIONS & RECOMMENDATIONS.....	116
6.1 Conclusions.....	116
6.2 Recommendations for future research	118
REFERENCES	120
APPENDIX	
A. List of publications resulting from this work	

LIST OF FIGURES, SCHEMES & TABLES

Figure	Page
Fig. 1.1. Schematic illustrating the performance of hybrid materials with polymers and ceramics.	2
Fig. 1.2. Schematics of the different types of nanocomposites based on I-O hybrid compounds.	2
Fig. 2.1. Schematic of hexagonally packed POSS units with alkyl side groups.....	8
Fig. 2.2. Schematic illustration of the packing structures of (a) flexible and (b) rigid POSS-imidazolium surfactants in the clay interlayers.....	17
Fig. 2.3. Cure profile and corresponding reaction mechanism of the catalyzed epoxy/anhydride system.....	22
Fig. 2.4. Bending modulus <i>vs</i> temperature curves for neat epoxy and POSS/epoxy at 95/5 and 75/25 (wt/wt) composites at (a) 120 °C/25 h; and post cured at (b) 150 °C/10 h.....	27
Fig. 3.1. DSC thermograms of (a) OB/HHPA; and (b) TGDDM/HHPA with catalyst/HHPA molar ratio of 0 (I), 0.009 (II) and 0.09 (III).....	48
Fig. 3.2. (a) Isothermal DSC thermograms of TGDDM/HHPA and OB/HHPA systems at 140 °C; and (b) conversion as a function of time for TGDDM/HHPA and OB/HHPA systems derived from (a).....	50
Fig. 3.3. (a) Typical dynamic DSC thermograms; (b) and their respective Arrhenius plots obtained by Kissinger and Ozawa methods for the OB/HHPA system.....	51
Fig. 3.4. Isothermal DSC thermogram of 5 mol.% OB/HHPA under the simulated pre-mixing condition, i.e. at 110 °C.	53

Fig. 3.5. Evolution of the FTIR spectrum of 5 mol.% OB/HHPA during the pre-mixing reaction.....	54
Fig. 3.6. Evolution of SEC chromatograms of a 5 mol.% OB/HHPA reaction mixture in Stage I; the inset is the mass distribution curves.	55
Fig. 3.7. SEM micrographs of the fractured surfaces of 5 mol.% OB hybrid materials with various pre-mixing times: 0 min (A and D), 10 min (B and E), 20 min (C and F).	57
Fig. 3.8. DSC thermograms depicting T_g s of the hybrids containing 5 mol.% OB at different pre-mixing times. The resins were cured at 140 °C for 1 h and post-cured at 200 °C for 24 h.....	58
Fig. 3.9. (a) DSC thermograms depicting T_g s of the hybrids containing 5 mol.% OB (pre-mixing time = 10 min) at different post-cure times. (b) T_g s of the hybrids as a function of post-cure time.....	59
Fig. 3.10. SEM micrographs of the fractured surfaces of (A) 5, and (B) 10 mol.% OB-10 hybrid networks.	61
Fig. 3.11. Storage modulus E' as a function of temperature for (a) TGDDA/HHPA; (b) 5 mol.% OB-10; (c) 5 mol.% OB-10-H; (d) 10 mol.% OB-10; (e) OB/HHPA; (f) OB/HHPA-H.....	62
Fig. 3.12. FTIR spectra of (a) OEpPOSS; and (b) OAPS.....	67
Fig. 3.13. SEM micrographs of hybrids with increasing POSS-anhydride content: (A) 5; (B) 10; and (C) 15 mol.% OEpPOSS.....	68
Fig. 4.1. Dynamic DSC thermograms and their respective Arrhenius plots for the ECHM/HHPA (A and B); and ECHM/HHPA/POSS-IMC systems (C and D).	79
Fig. 4.2. FTIR spectra of (a) POSS-IMC; (b) ECHM/HHPA/POSS-IMC mixture; and (c) its resultant resin. The peak intensities are not adjusted for clarity.....	82
Fig. 4.3. DSC thermograms of (a) ECHM/HHPA; (b) ECHM/HHPA/POSS-IMC; and (c) ECHM/HHPA/POSS-MMT mixtures at a heating rate of 10 °C/min.	83
Fig. 4.4. WAXS patterns of (a) POSS-IMC; (b) H-POSS-IMC; (c) Na-MMT; (d) POSS-MMT; and (e) H-POSS-MMT. The intensity of the curves is not adjusted for clarity.	84

Fig. 4.5. SEM micrographs of the fractured surfaces of H-POSS-IMC showing irregular shaped POSS domains (white regions) at low (A) and high (B) magnifications.....	85
Fig. 4.6. TEM micrographs (A to E) of H-POSS-IMC resin.....	86
Fig. 4.7. Schematic illustrating POSS-IMC aggregation states in H-POSS-IMC resin. ...	86
Fig. 4.8. Polarized optical micrographs of POSS-MMT pre-mixed with ECHM at 50 °C for 0 h (A); 8 h (B); and 20 h (C).....	87
Fig. 4.9. TEM micrographs (A to C) of H-POSS-MMT resin.....	88
Fig. 4.10. Schematic illustrating the clay intercalation states in H-POSS-MMT resin.	89
Fig. 4.11. (A) Storage moduli E' and (B) loss moduli E'' as functions of temperature for (a) ECHM/HHPA; (b) H-POSS-IMC; and (c) H-POSS-MMT. Magnified rubbery moduli E' curves are shown in the inset in (A).....	90
Fig. 5.1. MALDI-TOF-MS spectra of (a) OPS-Br; (b) OPS-13Br; and (c) OBPS with Ag^+ matrix.	97
Fig. 5.2. WAXS patterns of the POSS fillers and their corresponding hybrids.....	104
Fig. 5.3. SEM micrographs of fractured surfaces of unbonded POSS hybrids with 5 wt.% OPS (A and B); OPS-Br (C and D); OBPS (E and F); OPS-13Br (G and H).	105
Fig. 5.4. TEM micrographs of 5 wt.% OPS-13Br (A to D).....	106
Fig. 5.5. DSC thermograms showing the T_g s of (a) TGDDM/HHPA; (b) 5 wt.% OPS; (c) 5 wt.% OPS-Br; (d) 5 wt.% OBPS; and (e) 5 wt.% OPS-13Br resins.....	108
Fig. 5.6. (a) Storage moduli E' and (b) loss moduli E'' as functions of temperature for the unbonded POSS hybrid resins.	109
Fig. 5.7. 3-dimensional molecular models of (a) OPS-Br; and (b) OPS-2Br nano-fillers in 5 wt.% OPS-Br hybrid using CS Chem3D with MM2 energy minimization. The lengths are estimated from the diagonal apexes of the molecules.....	110

Fig. 5.8. TGA thermograms of the epoxy/POSS hybrids under (a) nitrogen; and (b) air atmosphere (– TGDDM/HHPA; ■ 5 wt.% OPS; ○ 5 wt.% OBPS; ▲ OPS; ◇ OBPS).112

Scheme	Page
Scheme 2.1. Typical structure of T ₈ POSS.	7
Scheme 2.2. Typical hydrosilylation reaction of POSS.	9
Scheme 2.3. Methods of incorporating POSS into polymer matrices. The last method depicts the direct cross-linking of POSS units.	12
Scheme 2.4. Structure of 2:1 layered silicates.	14
Scheme 2.5. Structure of the three-membered oxirane ring.	17
Scheme 2.6. Structures of (a) TGDDM; and (b) ECHM epoxies.	19
Scheme 2.7. Structures of (a) HHPA; and (b) EPICLON.	20
Scheme 2.8. Cure mechanism of a catalyzed epoxy-anhydride system.	20
Scheme 2.9. Tether structures of (a) OG; and (b) OC.	28
Scheme 2.10. Chemical structure of partially condensed POSS with the types of non-reactive tethers used in the studies.	30
Scheme 3.1. Hydrosilylation reaction routes for (a) OB; and (b) OG.	41
Scheme 3.2. Epoxidation route for OE.	42
Scheme 3.3. Chemical structures of (a) OB; (b) OG; (c) OE; (d) TGDDM; (e) HHPA; and (f) 1H-imidazole.	43
Scheme 3.4. Schematic cure mechanism of catalyzed epoxy-anhydride system.	49

Scheme 3.5. (a) OB oligomer formation as a function of pre-mixing time; and (b) the chemical structure of a dimer, i.e. two OB molecules attached to a HHPA molecule, formed in Stage I.....	56
Scheme 3.6. Interaction between POSS of different tether lengths with HHPA molecules.	64
Scheme 3.7. Idealized synthesis route for the POSS-anhydride, OEpPOSS.	66
Scheme 4.1. Structures of (a) POSS-IMC; (b) POSS-MMT; (c) ECHM; and (d) HHPA.	75
Scheme 4.2. The proposed catalytic mechanism of the POSS-imidazolium for epoxy-anhydride system.	81
Scheme 5.1. Chemical structures of (a) OPS; (b) OPS-Br; (c) OBPS; (d) OPS-13Br; (e) TGDDM; and (f) HHPA.	98

Table	Page
Table 3.1. Compositions and curing conditions for preparation of the hybrid networks.	44
Table 3.2. Peak exotherm temperatures (T) at different heating rates (q) and the corresponding activation energies (E_a) of the TGDDM/HHPA and OB/HHPA systems.	52
Table 3.3. Summary of thermal and thermo-mechanical properties of the epoxy hybrids.	60
Table 3.4. Peak exotherm temperatures (T) at different heating rates (q) and the corresponding activation energies (E_a) of the OB/HHPA and OG/HHPA systems.	63
Table 3.5. Summary of thermal properties of the hybrids with different POSS tether length. The hybrids were cured for 1 h at 140 °C in air and post-cured for 72 h at 200 °C in argon.	65
Table 3.6. Summary of thermal and thermo-mechanical properties of the POSS-anhydride epoxy hybrids.	68

Table 4.1. Compositions and cure conditions of H-POSS-IMC and H-POSS-MMT networks.....	76
Table 4.2. Peak exotherm temperatures (T) at different heating rates (q) and the corresponding activation energies (E_a) of the ECHM/HHPA and ECHM/HHPA/POSS-IMC systems.	80
Table 4.3. Summary of thermal and thermo-mechanical properties of the neat and hybrid resins.	91
Table 5.1. Molar vaporization energies (U) and molar volumes (V) of the chemical groups.....	100
Table 5.2. Calculated Hildebrand parameters of the individual resin components.	102
Table 5.3. CTE of the hybrid resins in different temperature ranges.	111
Table 5.4. Summary of thermal degradation data from the TGA curves.	112
Table 5.5. Static contact angles (θ) and free surface energies (γ_s) of the epoxy hybrids.	114
Table 5.6. Elemental compositions of 5 wt.% OBPS resin determined by XPS.	114

LIST OF ABBREVIATIONS & ACRONYMS

CEC	cationic exchange capacity
CTE	coefficient of thermal expansion
DSC	differential scanning calorimetry
DMA	dynamic mechanical analysis
E'	storage modulus
E''	loss modulus
E_a	activation energy
ECHM	3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate
FTIR	Fourier transform infrared
HPHA	hexahydrophthalic anhydride
MALDI-TOF-MS	matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy
MDSC	modulated differential scanning calorimetry
MMT	montmorillonite clay
OB	octakis(dimethylsiloxybutyl epoxide) octasilsesquioxane
OBPS	octa(bromophenyl) octasilsesquioxane
OG	octakis(dimethylsiloxyglycidyl epoxide) octasilsesquioxane
OE	octakis(dimethylsiloxy epoxide) octasilsesquioxane
OPS	octa-phenyl POSS
POM	polarizing optical microscopy
POSS	polyhedral oligomeric silsesquioxane

POSS-IMC	1,2-dimethyl-3-(benzyl heptaisobutyl POSS) imidazolium chloride
SEC	size exclusion chromatography
SEM	scanning electron microscopy
T_g	glass transition temperature
T_d	thermal degradation temperature
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
TGDDM	<i>N,N,N',N'</i> -tetraglycidyl-4,4'-diaminodiphenyl methane
TMA	thermo-mechanical analysis
WAXS	wide angle X-ray spectroscopy
XPS	X-ray photoelectron spectroscopy

ABSTRACT

This work is focused on the effect of polyhedral oligomeric silsesquioxane (POSS) compounds bearing reactive and non-reactive groups on the properties of resultant epoxy-anhydride hybrids and the underlying mechanisms. With rapid developments in nanotechnology, there has been great interest in polymer nanocomposites such as epoxy-based hybrids. POSS compounds have been incorporated in amine-cured epoxies for property improvements. In contrast, POSS/epoxy hybrids based on anhydride cure agents are seldom studied due to challenges such as the kinetically-controlled cure process and the requirement of catalysts for effective curing which may lead to complex reaction kinetics. However, the benefits of longer pot lives, better controlled curing, higher thermal and dimensional stabilities may outweigh the detriments.

Kinetics, morphological and thermal studies were carried out to elucidate the effect of a POSS-epoxy on the properties of an epoxy-anhydride system in which the epoxy has self-catalytic sites. The POSS tether length difference on the cure kinetics was investigated. Tailoring POSS tether chemistry to reduce the cure kinetics difference between resin components was also studied with a novel POSS-anhydride. Anhydride-cured epoxy hybrids containing POSS-imidazolium (POSS-IMC) surfactants and corresponding modified clays have been prepared. Their catalytic effects were examined with correlation to the resultant morphologies and impact on the thermal properties. Interfacial interactions of non-reactive POSS on the thermal properties of epoxy-anhydride hybrids have also been investigated with octa-phenyl POSS (OPS) and its brominated derivatives.

The incorporation of POSS-epoxy implicates the cure kinetics, largely due to competing epoxy-anhydride pairs, causing incomplete cure and inhomogeneity in the network. Shorter POSS tethers resulted in slower cure due to increased steric hindrance. Promising improvements in properties were obtained when POSS-anhydride was used, which effectively eliminated the competing epoxy reaction pairs. The catalytic effect of POSS-IMC was demonstrated by the lowering of the activation energy in the modified epoxies over the neat resins. The resultant POSS-IMC hybrid shows improved glassy modulus due to the reinforcing effect of the pendent POSS-IMC units. Incorporation of the corresponding modified clays enhances the glassy modulus further, with ~20 % increase with only 2.3 wt.% POSS-imidazolium modified clay. Electron microscopy data and X-ray diffraction analysis confirmed that the dispersion of non-reactive POSS is dependent upon their compatibility with the epoxy matrix. Thermogravimetric analyses reveal the synergistic effects brought about by the brominated OPS with increase in thermal stability and mass loss retardation.

1 INTRODUCTION

Nanotechnology is recognized in the scientific communities and high tech industries as one of the most promising avenues of technology for advanced applications in the 21st century. Ever burgeoning research interests are being fostered by the constant need for technology breakthroughs as many new applications are being developed each year. Rapid developments in many aspects of nanotechnology have been made such as in the area of polymer nanocomposites.

Polymer nanocomposites are polymers reinforced by fillers that have one or more dimensions in the nanometre length scale. Some of these nano-fillers incorporated in polymer nanocomposites include carbon nanotubes, nano-silica, layered silicates and metal nanoparticles. As the size of the fillers approach nanometre scale, the nanocomposite properties are mainly affected by the interfacial interactions between the matrices and the fillers rather than the bulk properties.

The relationship that arises from these filler-matrix interactions presents opportunities for tailoring the characteristics of the fillers to improve compatibility with the matrices. In this bottom-up approach, it usually involves the modification of the inorganic fillers with organic components to better suit the organic nature of the polymer matrices. They are usually known as inorganic-organic (I-O) hybrid compounds.

These I-O hybrid compounds have garnered enormous research interest as they possess synergistic combinations of constituent properties, providing superior global properties to the nanocomposites over traditional ceramics and polymers (Fig. 1.1). Several classes of nanocomposites based on I-O hybrid compounds have been developed, depicted in Fig. 1.2, such as sol-gel networks i.e. three-dimensional cross-linked systems

with a dispersed inorganic phase in the polymer matrix; pre-ceramic polymers such as polycarbosilanes, polysiloxanes and polysilanes; and inorganic/organic polymer blends [1].

Fig. 1.1. Schematic illustrating the performance of hybrid materials with polymers and ceramics.

Fig. 1.2. Schematics of the different types of nanocomposites based on I-O hybrid compounds [1].

Another class of I-O hybrid compounds have been developed based on polyhedral oligomeric silsesquioxanes (POSS). They are uniquely distinct from other types of hybrid compounds in that they are highly customizable. The organic substituents on the POSS can be tailored with almost any type of chemical groups, enabling the POSS compounds to be compatible with a very wide range of polymer matrices. POSS have been applied to numerous polymeric matrices such as polystyrenes, polypropylenes, poly methyl methacrylates, polyimides, polyurethanes, and epoxies [1-5]. More recently, POSS have also been used as clay intercalating agents for preparing polymer/clay nanocomposites [6-14].

Epoxies are one of the most important engineering thermosetting materials in use in many industries today due to their good engineering properties upon cure. They are widely used in the aerospace and automotive industries as adhesives, coatings and composite matrices, structural building materials in clean energy, as well as packaging and encapsulant materials in the electronics industry [15]. Thus, there has been much research interest over the years to try to incorporate POSS into epoxies to improve the properties of the resins [16-73].

Epoxies are usually copolymerized by curing agents such as amines and anhydrides to form cross-linked networks. Anhydride curing agents are generally preferred over amines for some applications such as electronics as the resultant epoxy formulations have a longer pot life since they do not react with epoxy at room temperatures unless catalyzed by other chemicals. Their reactions with epoxies can be controlled and tailored to suit specific needs. Anhydride-cured epoxies are generally of higher thermal stability than amine-cured epoxies due to the allylic ether C–O bond being more stable than allylic amine C–N bond. They also have better electrical insulation properties such as dielectric constant, low shrinkage, and stress-free systems than amine type hardeners [15]. Some

potential applications for POSS modified anhydride-cured epoxies include high strength structural materials such as wind turbine blades, aircraft and automobile chassis, and ‘no-flow’ encapsulant materials in electronics industries.

However, the main challenge with anhydride-cured epoxies is that the cure process is controlled by kinetics of the ring-opening reactions of epoxy and anhydride, thus the cure to completion is more difficult than that of amine-cured epoxies. Often, catalysts have to be used to bring the cure down to more manageable temperatures. Hence, reaction kinetics between the POSS compounds and epoxy monomers will play a major role in the preparation of POSS modified anhydride-cured epoxy nanocomposites. To mitigate any detrimental effects brought about by cure kinetics, it is worth to study the incorporation of functional POSS compounds bearing multiple and single reactive groups as well as non-reactive groups to establish an understanding of the roles they play in shaping the properties of the resultant nanocomposites.

To date, most studies on POSS/epoxy nanocomposites are mainly on the use of amine-based cure agents [16-31, 33-73]. There is a dearth of publications on anhydride-cured POSS/epoxy nanocomposites [30].

1.1 Objectives

The major goal for this work is to understand how the incorporation of POSS compounds functionalized by reactive and non-reactive groups affects the properties of the epoxy-anhydride hybrids, and the roles played by reaction kinetics.

The thesis aims to present the following aspects:

1. *To investigate the effect of cure kinetics between functional POSS bearing multiple reactive groups and an epoxy resin cured with an anhydride on the thermal and thermo-mechanical properties of the resultant hybrids.*

POSS containing multiple reactive groups generally take part in network formation via covalent bonding and act as chemical cross-link junctions. To establish the structure-property relationship, it is important to understand how the reaction kinetics between different components will affect the cure of the hybrid resins and the impact on the resin properties.

2. *To study the catalytic effect of mono-functional POSS bearing a reactive group on the resultant morphologies and the consequential thermal and thermo-mechanical properties of POSS/epoxy and POSS modified clay/epoxy nanocomposites.*

Mono-functional POSS bearing a reactive group that can catalyze the cure of the epoxies are of interest as they have synergistic functions. They are able to initiate the cure of epoxy-anhydride resin at lower temperatures and can act as reinforcing agents. It will be particularly useful for the intercalation of layered nano-silicates. When attached to the clay surface, it is hypothesized that the mono-functional POSS may be able to initiate cure of the epoxy monomers within the clay and help to facilitate dispersion of clay and influence the resultant thermal properties.

3. *To study the effect of incorporation of functional POSS bearing non-reactive groups on the dispersion and resultant thermal properties of the anhydride-cured epoxy hybrids.*

The dispersion of non-reactive POSS is to a very large extent determined by the compatibility of the nano-fillers with the matrix. Hence, it is essential to study how the compatibility between the POSS and matrix affect the dispersion of the fillers and also the consequences on the thermal properties of the resins.

1.2 Organization of thesis

Chapter 2 reviews past literature on topics of interest pertaining to this work. Chapter 3 discusses the effect of cure kinetics on the resultant morphologies, thermal and thermo-mechanical properties when reactive POSS is incorporated into an anhydride-cured epoxy resin. Chapter 4 details the discussion on the catalytic effect of a mono-functional reactive POSS on the morphological structures of resultant novel anhydride-cured POSS/epoxy and POSS modified clay/epoxy hybrids and the consequential implications on the thermal and thermo-mechanical properties. Chapter 5 deals with the effect of compatibility of functional POSS with non-reactive groups on filler dispersion and the resultant homogeneity and thermal properties in novel POSS-filled epoxy hybrids.

The main findings and conclusions for this work and future recommendations are presented in Chapter 6. The appendix lists the publications that resulted from this work.

2 REVIEW OF LITERATURE & THEORY

2.1 Polyhedral Oligomeric Silsesquioxanes (POSS)

2.1.1 Structure of POSS

The term silsesquioxane refers to all structures with the empirical formula of $(\text{RSiO}_{1.5})_n$ where $n = 8, 10, 12$ and R is hydrogen or any alkyl, alkylene, aryl, arylene, or organo-functional derivatives of the aforementioned groups. First isolated by Scott in 1946 [74], silsesquioxanes are derived mainly from the hydrolysis and condensation of tri-functional organo-silanes. For the purpose of this work, the review will concentrate on POSS based on the $(\text{RSiO}_{1.5})_8$ formula, also known as T_8 POSS.

Scheme 2.1. Typical structure of T_8 POSS.

An individual unit of T_8 POSS, with a size of about 0.53 nm diagonally, comprises of an inner inorganic rigid core made up of 8 silicon and 12 oxygen atoms in a cage-like cubic structure that can be externally covered by organic substituents shown in Scheme 2.1. The POSS cubes can be considered as the smallest possible particles of silica in

2.1.2 POSS chemistry

The uniqueness of POSS which differ from traditional silica, silicones and other fillers is that the POSS cages can be functionalized with a wide variety of reactive and non-reactive groups. Types of starting POSS materials that are often used for modification to prepare a wide range of functionalized POSS compounds include T_8H_8 , $T_8[OSiMe_2H]_8$, $T_8[OSiMe_2CH=CH_2]_8$, $T_8[CH=CH_2]_8$, T_8Ph_8 , $T_8[ONMe_4]_8$, and $T_8[(CH_2)_3NH_2]_8$. One of the most common routes to synthesize functionalized POSS is *via* a simple hydrosilylation reaction in the presence of a platinum catalyst (Scheme 2.2).

Scheme 2.2. Typical hydrosilylation reaction of POSS.

This approach can be employed for POSS containing Si-H functionality and an organic compound bearing unsaturated groups. For example, $T_8[OSiMe_2H]_8$ can be hydrosilylated with 1,2-cyclohexene epoxide [17], allyl glycidyl ether [76] and epoxy-5-hexene [77] to form POSS with reactive epoxy groups that can be used for preparing epoxy nanocomposite networks. T_8H_8 compounds may also be reacted with terminal alkenes of varying hydrocarbon chain length to form POSS compounds with alkyl groups [78]. They can be added to polymer nanocomposites as molecular silica. Unsaturated anhydrides such as maleic anhydride can also be reacted *via* hydrosilylation with POSS to

prepare compounds with anhydride functionalities [79]. These POSS-anhydride compounds have potential for use as curing agents for epoxies.

Vinyl POSS such as $T_8[CH=CH_2]_8$ and $T_8[OSiMe_2CH=CH_2]_8$ are able to undergo addition reactions with *m*-chloroperoxybenzoic acid for epoxidation of POSS, although complete epoxidation can only be achieved in the latter as reported by Zhang *et al.* [80].

$T_8[(CH_2)_3NH_2]_8$, functionalized with free amines from the solvolysis of $H_2N(CH_2)_2Si(OEt)_3$ in a basic medium, can be used as cure agents for epoxy network formation [81]. They can also be reacted with lactones to form compounds with biological binding affinities, and anhydrides to afford compounds with carboxylic acid functions [82-83].

Functionalization of phenyl groups on POSS, namely T_8Ph_8 or octa-phenyl POSS (OPS), allow for the preparation of a few useful derivatives. The phenyl rings are able to undergo nitration in cold fuming nitric acid for attachment of nitro groups to form octa nitrophenyl POSS [84]. Subsequent reduction of the nitro groups with formic acid and triethylamine yield a particularly useful POSS compound with free amine groups that can be used as curing agents for epoxies [49-51, 55]. The amine groups can be further imidized with anhydrides such as phthalic and maleic anhydrides to form POSS-imide monomers [84-85]. Direct bromination of the phenyl groups in T_8Ph_8 has also been reported [86-88].

The POSS can also be functionalized by substitution reactions directly at the cage or by corner-capping reactions of partially condensed POSS such as trisilanol POSS bearing seven non-reactive groups, usually alkyl or aryl groups, to yield mono-functional POSS with a single reactive group [89]. Some examples of groups that are attached to mono-functional POSS include hydroxyls, epoxides, amines, imidazolium salts, acrylates, norbornyls, aryl and alkyl groups.

The POSS chemistry is highly versatile, allowing almost limitless combinations of chemical groups to be functionalized to the POSS cores. For more comprehensive discussions on the synthesis and chemistry of the POSS, one can look up recent reviews by Lickiss and co-workers [82-83].

The high customizability of POSS allows them to be incorporated into an extensive range of polymers, biological matrices, and surfaces. The nature of the functionalized groups on POSS will determine the compatibility with the matrices.

2.1.3 Properties

Another major advantage of POSS is that they possess synergistic combination of properties listed below [1]:

- *High thermal stability* imparted by the robust inorganic Si-O cage which is less susceptible to decomposition at high temperatures.
- *Reduced heat evolution* during combustion due to the high silicon content in POSS.
- *Low density* due to the porous structure of the POSS cage.
- *Excellent corrosion and oxidation resistances* mainly due to the inorganic POSS core which is less susceptible to degradation in corrosive and oxidative environments.
- *Non-flammability and non-volatility*. Due to its predominantly inorganic nature, POSS do not burn. They instead formed a porous siliceous char upon thermal degradation. Since they do not burn, no volatiles are given off.
- *High solubility in many common solvents* when the POSS cubes are compatibilized with suitable organic tethers.

They have the potential to impart high glass transition temperatures (T_g s), improved thermal and thermo-mechanical properties, and good flame retardance when incorporated into polymeric materials.

2.1.4 POSS/polymer nanocomposites

POSS are usually investigated as reinforcing filler materials for enhancing the properties in polymer nanocomposites. There are mainly four ways to incorporate POSS compounds into polymeric materials. Scheme 2.3 depicts the methods of incorporating POSS into polymer matrices [83].

Scheme 2.3. Methods of incorporating POSS into polymer matrices. The last method depicts the direct cross-linking of POSS units.

The first method is to incorporate functionalized POSS with multiple reactive groups as cross-linking moieties in polymer matrices. Covalent bonds will be formed as the POSS undergo copolymerization reactions with the matrix monomers. The second method is the variation of the first, where the POSS, functionalized with a single reactive group, can be grafted onto the polymer chain ends as pendent units. The third method involves POSS containing non-reactive groups, and they are dispersed into the polymer by physical mixing as molecular silica fillers, mediated by either weak Van der Waals or strong polar interaction forces. The last method is the direct cross-linking of POSS units with multiple reactive groups to form POSS co-polymers.

A wide variety of POSS/polymer nanocomposites have been prepared to date. Some notable polymer systems include POSS-styryl, POSS-methacrylate, POSS-norbornyl, POSS-epoxy, POSS-polyimide, POSS-vinyl, and POSS-siloxane polymers [2-3].

2.2 POSS as intercalating agent in montmorillonite clay

2.2.1 Structure of montmorillonite clay

Layered silicates are essentially clay minerals consisting of thin layers bound together by counter-ions. The structure of layered silicates consists of tetrahedral sheets where the Si atom is surrounded by four O atoms, and octahedral sheets in where eight O atoms encompass a metal such as Al. In 2:1 layered silicates, the octahedral layer of alumina is sandwiched between two silica tetrahedra as shown in Scheme 2.4 [90]. The layer thickness of the clay sheet is around 1 nm and the lateral dimensions may range over several microns, resulting in very high aspect ratios. The structure of montmorillonite (MMT) is formed when in the 2:1 layered silicates, the Al cation in the octahedral layer is partially substituted by Mg cation. The overall negative charge of the MMT clay is

counter-balanced by Na and Ca cations that exist between the clay galleries. As these ions are unable to fit into the tetrahedral layers, the clay layers are held together by weak van der Waals and electrostatic forces, easily diminished by external polar forces like water, resulting in intercalation/exfoliation of the clay layers. As such, MMT clay portrays excellent properties like high cation exchange capacity (CEC) and good swelling ability, coupled with high aspect ratio and low cost, it is the most commonly used layered silicate today [91].

Scheme 2.4. Structure of 2:1 layered silicates [90].

MMT clay has been used as reinforcing agents in polymer nanocomposites over the past two decades as they may give rise to improved stiffness, strength and toughness when dispersed in polymers at the nano-scale [92]. MMT clay are structurally different from POSS in that they are sheet-like with large aspect ratios, which is essential for their

reinforcing efficiency. To disperse MMT clay into polymers, it is necessary to convert their hydrophilic surface to hydrophobic *via* cation exchange, where organic surfactants replace the inherent cations in the MMT.

2.2.2 POSS surfactants in clay/polymer nanocomposites

By functionalizing POSS with suitable organic surfactants, the hybrid surfactants can be used to improve the compatibility of the clay with polymers. The attractiveness of this approach resides in the large interlayer *d*-spacing brought about by the bulky POSS cages, which may help to improve clay intercalation/exfoliation in the polymer matrices, and the potential to impart synergistic effects of POSS and clay on property improvements. A number of research groups have studied POSS as clay modifiers and the properties of resultant POSS-clay/polymer nanocomposites [6-14].

Chang and co-workers have prepared polystyrene (PS)/montmorillonite nanocomposites based on aminopropylisobutyl POSS [6]. Single layer packing of the POSS-ammonium surfactants in the clay galleries are observed in WAXS analysis. Improved T_g s and thermal stability of the resultant POSS-modified clay/PS nanocomposites are reported. By using a long alkyl chain POSS-ammonium surfactant, C₂₀-POSS, they were able to increase the *d*-spacing of the clay layers in a later study [9]. Further improvement in the exfoliation of the clay is observed, with a maximum reduction in CTE by up to ~40 %.

He and Zhang prepared polyethylene (PE)/laponite clay nanocomposites based on octaaminopropyl POSS [7]. Exfoliation of the clay in PE is observed with significant improvements in storage modulus and thermal stability of the nanocomposites. Liu *et al.*

demonstrated some improvements in thermal stability with similar POSS-ammonium surfactant in montmorillonite/epoxy nanocomposites [14].

Bao's group reported a large increase in the interlayer d -spacing when aminopropylisooctyl POSS was used to modify montmorillonite clay, corresponding to a bi-layer packing arrangement of the POSS within the clay layers [10]. When incorporated in poly(cyclic butylene terephthalate), they discovered that the d -spacing of the clay did not improve upon addition of more than 0.4 CEC of POSS. In later studies on polypropylene and polyamide, similar bi-layer packing of aminopropylisooctyl POSS was observed [11, 13]. This led them to conclude that the d -spacing is strongly dependent on the arrangement of the POSS surfactant but less so on the POSS concentration. The simultaneous use of a second organic surfactant helps to improve exchange ratios, allowing more control over the hydrophobicity and polarity of the modified clays in the nanocomposites.

More recently, two novel POSS-imidazolium surfactants have been developed as potential clay modifiers [8, 12]. The clay modified with these POSS-imidazolium surfactants also exhibits large basal d -spacing owing to bi-layer packing of the POSS-imidazolium in clay interlayer. However, Toh *et al.* found that by incorporating more rigid POSS-imidazolium surfactants into clay, the bi-layer packing conformation will be more disordered as the degree of freedom is reduced. Higher thermal stabilities was also reported, plausibly due to low organic content and disordered structure that allow more ionically bonded POSS surfactants on clay [12].

Fig. 2.2. Schematic illustration of the packing structures of (a) flexible and (b) rigid POSS-imidazolium surfactants in the clay interlayers [12].

2.3 Epoxy resins

2.3.1 Epoxy structure

Epoxyes are chemical compounds that contain one or more of the three-membered oxirane rings shown in Scheme 2.5 [15]. They are thermosetting materials and will undergo copolymerization reactions with curing agents to form three-dimensional cross-linked networks. Due to the highly strained oxirane ring, the cure of the epoxy resins usually involves either the electrophilic attack of the O atom or the nucleophilic attack on one of the ring C atoms. Depending on the type of curing agent, the process can take place at room ambient or at elevated temperatures.

Scheme 2.5. Structure of the three-membered oxirane ring [15].

The chemical structure of epoxies has a bearing on the properties of the resultant resins. For example, the presence of glycidyl groups in the epoxies will impart flexibility to the resultant resins. As a result, viscosity decreases and the processibility improve. However, these aliphatic linkages also lower the thermal stability of the resins. Increased flexibility of the system will lead to the reduction in the glassy modulus and T_g s. To improve the thermal and thermo-mechanical properties of the cured resins, the use of epoxies with more rigid structures and high functionalities is adopted. Nevertheless, one must note that their use will consequentially lower processibility due to the reduction in the solubility and higher viscosities, thus a balance in the resin formulation must be considered. The incorporation of epoxies possessing rigid structures such as aromatic and cycloaliphatic rings is particularly useful in enhancing the thermal stability and char formation of the resins. The T_g s are also improved when more rigid epoxies are used as the degrees of freedom of the polymer chains are lowered in the cured resin, resulting in higher activation energies required for chain motions. Epoxies with higher functionalities allow for increased cross-linking densities which will have a positive impact on the T_g and modulus of the resultant epoxy resins.

The two epoxies used in this work are *N,N,N',N'*-tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) and 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate (ECHM), their structures given in Scheme 2.6. TGDDM was employed as it is widely used commercially to make high strength and performance composites due to its stiffness and high functionality i.e. $f = 4$. The phenyl rings contribute to the rigidity of TGDDM structure. Coupled with the high cross-linking density brought about by the four oxirane groups, good thermal properties and stability are expected when TGDDM is incorporated into the resin formulation. On the other hand, to study the catalytic effect of the POSS-imidazolium surfactant on the epoxy-anhydride reaction, an epoxy without any tertiary

amine sites that may compete with the reaction is essential, thus ECHM was selected for the study of POSS modified clay/epoxy systems. Albeit a low molecular weight difunctional epoxy, ECHM imparts some rigidity to the epoxy resin with the inclusion of its two cycloaliphatic oxirane rings which provide the steric hindrance. Between the two epoxies, TGDDM is expected to provide higher cross-link densities and thermal properties such as T_g and modulus because of its more rigid structure and higher functionality.

Scheme 2.6. Structures of (a) TGDDM; and (b) ECHM epoxies.

2.3.2 Cure chemistry in epoxy-anhydride system

There are many curing agents in use today such as amines and their derivatives, phenols, carboxylic acid functional polyesters and anhydrides, polysulphides and polymercaptans [15]. Of these, amines and anhydrides are the most common cure agents for the copolymerization of epoxies. Due to the challenges previously discussed in Chapter 1, such as the effect of reaction kinetics on the resultant properties in anhydride-cured POSS/epoxy systems and the fact that there was few studies done in this area, anhydrides are chosen as the cure agent of interest in this work.

The most common and important anhydride cure agents are cycloaliphatic in nature. There are many types of cycloaliphatic anhydride curing agents with different structures. The cycloaliphatic anhydrides used in this work are hexahydrophthalic anhydride (HHPA)

and 5-(2,5-dioxotetrahydrofurfuryl)-3-methyl-3-cyclohexyl-1,2-dicarboxylic acid anhydride (EPICLON) shown in Scheme 2.7.

Scheme 2.7. Structures of (a) HHPA; and (b) EPICLON.

Scheme 2.8. Cure mechanism of a catalyzed epoxy-anhydride system.

The cure mechanism for the catalyzed epoxy-anhydride system is illustrated in Scheme 2.8. During cure, the catalyst attacks and open the epoxy ring and form highly reactive alkoxide adducts. The reactive adducts are able to attack the anhydrides and form

carboxylate anion functional esters. These then react with more epoxy rings to form alkoxide esters and this alternating sequence leads to polyester formation and ultimately a cross-linked epoxy network.

The epoxy-anhydride system has been widely investigated over the last few decades. Guerrero *et al.* investigated the stoichiometry and cure of epoxy resins based on TGDDM and tetrahydrophthalic anhydride (THPA) [93]. They discovered that the optimum T_g is obtained when anhydride/epoxy ratio is around 0.8 to 0.9. Corcuera *et al.* studied the cure of TGDDM with HHPA in a series of studies [94-95]. It is found that an epoxy excess will result in higher reactivity of epoxy and anhydride monomers as there are more hydroxyl groups in the system. Cure kinetics analysis shows a first order reaction between TGDDM and HHPA.

In a study by Park and Lee [96], it is found that the cure profile of an epoxy-rich system comprising of diglycidyl ether of bisphenol A (DGEBA) and HHPA under the influence of an imidazole catalyst exhibits multiple peaks. As presented in Fig. 2.3, the lower temperature cure peak is assigned to the esterification reaction between the epoxy group and the anhydride whereas the higher temperature cure peak is attributed to the etherification reaction between epoxy groups i.e. homo-polymerization. The esterification reaction is a kinetically controlled process and the cure peak enlarges with increase in the catalyst concentration. At this stage, most of the anhydrides are consumed by reaction with the epoxies in the presence of the catalyst. As the reaction proceeds further, the distance between the functional groups increases, the process becomes diffusion-controlled. More energy in the form of higher temperatures is needed for the cure to proceed. This results in the second cure peak which is the etherification reaction.

Fig. 2.3. Cure profile and corresponding reaction mechanism of the catalyzed epoxy/anhydride system [96].

2.3.3 Properties and applications of anhydride-cured epoxies

The advantage that these anhydride agents have over amines is that they do not react with epoxies at room temperatures unless catalyzed by other chemicals, resulting in a longer pot life, which allows for more flexibility with the processing in terms of time and reworkability. Catalysts can be added to control the cure process of the epoxy-anhydride systems to suit specific requirements. When cured, it results in low shrinkage, stress-free systems [15]. Low shrinkage allows good dimensional accuracy in structural applications and allows for the manufacture of high strength adhesives with low residual stress. Anhydride-cured systems also have improved thermal stabilities over the amine-cured systems due to the allylic ether C–O bond being more stable than allylic amine C–N bond, enabling them to be used in high-performance applications. Anhydride-cured epoxies also have higher electrical insulation properties.

Anhydride-cured epoxies are critical in applications where controlling the precise cure at specified temperatures are required such as the electronics industries. Some of the applications include encapsulant materials in underfills for flip chips and outer protective materials for chips. Anhydride-cured epoxies are also used in electrical insulators where high dielectrics have to be used. Other common applications include high strength adhesives and structural building materials where there is little tolerance in dimensional accuracies such as aircraft and automobile parts.

2.3.4 Cure kinetics of epoxy-anhydride systems

The cure of epoxies with anhydrides is usually characterized by low exotherm reactions which require elevated temperatures for a long period of time. As such, catalysts such as tertiary amines and imidazoles are often used as activators to improve the cure rate by bringing the temperatures down to more manageable rates [15].

Work by Bouillon *et al.* has shown that imidazole catalysts are better than tertiary amines in the curing of epoxy-anhydride systems as they provide higher thermal stability [97]. Latent catalysts such as metal acetylacetonates [98] and imidazolium salts [99-100] have also been considered as high temperature latent catalysts for epoxy-anhydride cure. They are usually used in formulations where cure is required at elevated temperatures but no curing takes place at the room temperature, thus improving the pot life. Imidazolium salts are of particular interest in this work as they are shown to be able to functionalize with the POSS cage [8, 12]. When incorporated in epoxy-anhydride systems, the resultant POSS-imidazolium surfactants may have catalytic effect on the epoxy cure when they decompose into imidazole moieties at elevated temperatures.

Besides the use of external catalysts to enhance the cure rate of the epoxy-anhydride system, epoxies with self-catalyzing effect such as amino-glycidyl epoxies can also be employed to lower the cure temperatures. Rocks *et al.* studied the cure kinetics between TGDDM, an amino-glycidyl epoxy containing two internal tertiary amine sites, and maleic anhydride and pyromellitic dianhydride [101]. They found that unlike other high-temperature curing epoxy-anhydride systems, the cure starts at room temperature. It is attributed to the internal tertiary amine sites that provide the catalytic sites which may have catalyze the ring-opening of the anhydrides (Scheme 2.6).

2.3.5 Kinetic models

As the reaction between epoxies and anhydrides is predominantly kinetically controlled, the cure kinetics of epoxy-anhydride systems are more complicated than amine-cured epoxies. The addition of catalysts to enhance the cure rate will further complicate the cure kinetics of the system.

Barton reviewed the cure kinetics of epoxy-anhydride systems and noted that some of the systems have reactions corresponding to first order but most of the systems are fractional and it is impossible to relate them to a simple reaction mechanism [102].

In this work, two very common dynamic kinetic models are deployed, the Kissinger and the Flynn-Wall-Ozawa models [103-105]. The advantage is that both models do not require prior knowledge of the reaction mechanism, and yet provide data on the kinetics between different components in the system. According to Kissinger model, the activation energy can be obtained from the equation below [106],

$$\frac{d[\ln(q/T_{\text{peak}}^2)]}{d(1/T_{\text{peak}})} = -\frac{E_a}{R} \quad (2.1)$$

where T_{peak} is the peak exotherm temperature, q the constant heating rate, E_a the activation energy of the reaction, and R the universal gas constant. The value of E_a can be obtained by plotting $\ln(q/T_{\text{peak}}^2)$ versus $1/T_{\text{peak}}$.

The Ozawa method yields a simple relationship between the activation energy E_a , heating rate q , and the iso-conversion temperature T , giving the activation energy as:

$$E_a = \frac{-R}{1.052} \frac{\Delta \ln q}{\Delta(1/T)} \quad (2.2)$$

Similarly, the E_a can be derived from the slope of $\ln q$ versus $1/T$ plot. Higher the E_a , slower the kinetics of the particular component in the system.

2.4 Epoxy Nanocomposites

Epoxyes are one of the most important engineering thermosetting materials used in many industries today. Naturally, many studies have been made to incorporate epoxyes with nano-fillers to allow for exponential improvements in properties to accommodate ever more demanding applications. Different types of nano-fillers in epoxyes have been explored such as carbon nanotubes and nanofibres [107], nano-layered silicates [108] and nano-silica particles [109].

The chemistry of the fillers has an effect on the kinetics of the epoxy systems which in turn affect the resultant properties of the resins. For fillers bearing groups that are able to react with the resin monomers, when incorporated into epoxyes, they are able to take

part in network formation by covalent bonding to the matrix. Depending on the number of reactive functionalities, the fillers may be incorporated as pendent units on the polymer backbone or as chemical cross-link junctions. They act as nano-reinforcing agents, hindering network chain motion due to external stresses.

As the fillers take part in the copolymerization reaction, the reaction kinetics between fillers and the epoxies will play a major role in determining the properties of the resultant nanocomposites. For example, if the fillers attached with reactive epoxide groups have slower kinetics than the base epoxy; poor dispersion of the fillers will result as the base epoxy will consume the curing agent at a much faster rate. Many of the fillers will be left un-reacted and plasticization of the network will occur, leading to poorer thermal and thermo-mechanical properties. The larger the kinetics difference between resin components, the poorer the properties will be. For fillers with non-reactive groups, compatibility between the fillers and the matrix will play a more dominant role than the cure kinetics in determining the resultant properties of the nanocomposites. In this work, three kinds of POSS filler compounds bearing multiple and single reactive groups, and non-reactive groups, in epoxy-anhydride systems are studied.

2.5 POSS/epoxy nanocomposites

2.5.1 POSS as cross-linkers

POSS units bearing multiple reactive groups have been widely studied as cross-linkers in epoxy resins [16-55]. The attractiveness of these POSS with multiple reactive groups as cross-linkers is that they are able to bond covalently with the resin molecules during network formation, and act as chemical cross-link junctions, potentially increasing the cross-linking density of the networks.

Li *et al.* studied the effect of POSS containing epoxy groups in epoxy nanocomposites by varying the weight fractions of POSS [16]. They found that at $T < T_g$, the resulting dynamic modulus of epoxy nanocomposites with high POSS content is lower than that of neat epoxy, but increased when $T > T_g$ (Fig. 2.4). After post-curing, T_g of the POSS/epoxy nanocomposites increased due to improved cross-linking density.

Fig. 2.4. Bending modulus vs temperature curves for neat epoxy and POSS/epoxy at 95/5 and 75/25 (wt/wt) composites at (a) 120 °C/25 h; and post cured at (b) 150 °C/10 h [16].

Laine *et al.* studied the effect of tailoring the organic tether architecture on the global properties of the POSS/epoxy nanocomposites based on two POSS octa-functionalized cubes, one with a more flexible glycidyl tether (OG), and the other of more rigid ethylcyclohexenyl tether (OC), cured with diamino diphenyl methane (DDM) hardener [17]. It was found that the OC/DDM nanocomposite has poorer fracture toughness but higher elastic modulus than the OG/DDM resin due to poor flexibility of the cycloaliphatic ring structure in OC tethers at molecular level revealed by modelling studies (Scheme 2.9). They concluded that small changes in the architecture of the organic tethers play an important role in determining the properties of the nanocomposites.

Scheme 2.9. Tether structures of (a) OG; and (b) OC.

By varying formulation ratios, it was found that the global properties of the epoxy resins can be tailored in a report by Choi *et al.* [18]. It was observed at NH_2 group/epoxy group ratio N is 0.5, where each DDM molecule is believed to react with four OG cubes, the cross-linking density is the highest. These findings concurred with a later study done by Mya's group [23]. The latter's group explored the thermal stability and thermo-mechanical properties of two octa-functionalized cubes, OG and octakis(dimethylsiloxylbutyl epoxide) octasilsesquioxane (OB), cured with an dicyclopentadiene hardener. The thermal stabilities of the hybrids are shown to be the highest at N ratio = 0.5. The hybrids also showed improved thermal properties over the control resin.

Pellice *et al.* found that using POSS with bulky and flexible organic substituents topped with secondary hydroxyls in each tether, the T_g decreases due to the flexibility of the organic tethers in addition to the reduction in the cross-linking density [19]. The mechanical properties such as yield stress and elastic modulus improve due to the increase in the cohesive energy density produced by hydrogen bonding through the hydroxyl groups.

Zheng's research group performed a few studies with POSS cubes of different tether architecture and discovered that the T_g s are dependent on the content of POSS in the nanocomposites [25, 27, 50]. At low POSS loadings, the T_g s are enhanced but drop when the loading increases. They postulated that there are two competitive factors. On one hand,

the increase in T_g s can be attributed to the nano-reinforcement effect of the POSS on the epoxy matrix, restricting polymer chain motions. On the other hand, the bulky POSS cages are able to act as plasticizers. As POSS loading increases, the latter effect is more dominant, giving rise to reduced T_g s. Their data suggests that tether architecture and POSS interactions with the epoxy matrices play critical roles in determining the resultant properties of the nanocomposites.

Sheng's group studied the degree of cross-linking, pore size distribution, effects of linker length, tether rigidity, and the number of reactive tethers *via* continuous-space Monte Carlo simulations [22]. It is found that the cross-linking density and inter-cubic pore size increase when linker length increases. Networks incorporated by POSS with rigid tethers will have a lot of un-reacted free tethers due to steric hindrance, resulting in low cross-linking density.

Chen *et al.* studied the effect of cure kinetics of amine-cured POSS/epoxy nanocomposites on the resultant resin properties and found that the activation energy of the POSS/epoxy is higher than that of the neat composite i.e. poorer cure kinetics [21]. As a result, some of the POSS are left un-reacted in the resin after vitrification, lowering the initial decomposition temperature of the hybrid. They believed that the un-reacted POSS in the resin may have formed POSS aggregates and act as plasticizers, lowering the network homogeneity and ultimately the thermal properties. In a later study, they sought to improve the homogeneity by introducing a soft epoxy with reduced reactivity, thereby reducing the kinetics difference between the resin components [31]. As a result, the POSS dispersion was improved, leading to enhanced thermal properties. The combined use of small molecule curing agents such as dicyandiamide and a phosphorous-containing compound for the cure of POSS-epoxy hybrids to improve the homogeneity was also demonstrated in a separate study by Liu *et al.* [28].

Several studies have shown that the impact toughness of the epoxy resins is enhanced with the incorporation of small amounts of POSS cross-linkers into the networks [20, 35, 43-44]. The formation of the chemical cross-link junctions by the POSS units in the network leads to the formation of nano- and micro-voids which improve the impact yield strength of the resins.

POSS when degraded is able to form an inert siliceous layer that is able to protect the epoxy resin bulk from further decomposition as shown by Zhang *et al.* [52]. The retention of mechanical properties of the epoxy hybrids after degradation was also reported to increase with POSS loading.

POSS based on partially condensed cage structure have also been studied as potential cross-linkers in epoxy resins with varied improvements in thermal properties [46-48]. The types of non-reactive groups tethered to the POSS structures will give different degree of compatibility with the epoxy matrices (Scheme 2.10). Better compatibility of POSS with the matrix, higher the thermal properties of the hybrids.

Scheme 2.10. Chemical structure of partially condensed POSS with the types of non-reactive tethers used in the studies [47-48].

Apart from the possibility of replacing epoxies, POSS have also been studied as potential hardeners for the cure of epoxies [49-55]. Laine's group prepared POSS/epoxy

nanocomposites utilizing POSS cages with rigid and thermally stable aromatic amine tethers as curing agent [49]. Comparing with OG, they found that the aromatic tethers of the POSS, octa(aminophenyl) octasilsesquioxane (OAPS), are able to further increase the char yields and the decomposition temperatures. The short length and structure of the aromatic tethers also helped to reduce tether relaxation motions, thus stiffening the network and increasing T_g . Optimal thermal properties are only obtained when the NH_2 /epoxy group ratio $N = 1$, in contrast to the data reported by Choi's and Mya's groups [18, 23]. This is due to the fact that amine groups are attached to the nano-sized POSS cage, increasing the steric hindrance with the epoxy molecules. When $N = 0.5$, only one epoxy group is able to react with one N-H functionality, obscuring the other N-H group from reacting with another epoxy. This will lead to incomplete cure of the network. When $N = 1$, less epoxy groups will be left un-reacted as most of them will be able to access the NH_2 groups on the POSS cages, leading to improved thermal properties.

They have also developed a novel class of epoxy hybrids using a rigid tetraglycidyl *m*-xylenediamine epoxy with OAPS as the curing agent, achieving very low coefficient of thermal expansion (CTE) values [51]. Other studies have shown that epoxies cured by POSS curing agents exhibit improved thermal degradation characteristics [52-53, 55].

More recently, Perrin *et al.* have demonstrated that when POSS is functionalized with suitable organic groups such as quaternary ammonium groups, it is able to perform multiple roles, that of a cross-linker and a catalyst [40]. It was found that the POSS is able to catalyze the epoxy-amine cure but with limited cross-linking, as the termination reactions severely compete with the propagation reactions.

2.5.2 Pendent POSS as a reinforcing agent

POSS containing a single reactive group have also been investigated as potential reinforcing agents for epoxy resins [56-70]. They are incorporated as pendent POSS units attached at the polymer chain ends within the networks, able to potentially hinder polymer chain motions by acting as physical cross-link points.

Lee and Lichtenhan investigated the effect of mono-functional reactive POSS on the viscoelastic properties and dimensional stability of the epoxy thermosets [56-57]. They observed that T_g increases with POSS content. A broader glass transition region is also observed, suggesting that the presence of the rigid POSS cages helped to slow the transition from the glassy to the rubbery state by hindering the polymer chain motions. Creep resistance also improved with the relaxation motion of the network chains effectively retarded, likely due to the nano-size and mass of the POSS cages.

Abad *et al.* investigated the compatibility of the epoxy networks with high mono-functional POSS content [58]. It was found that by mixing mono-functional reactive POSS units with isobutyl groups into an epoxy network with aromatic characteristics decrease the filler-matrix compatibility, resulting in macro-phase separation. Polymerization-induced phase separation was also detected during network formation, producing small and dispersed POSS domains. The higher T_g observed is attributed to the formation of pendent POSS structures on the polymer chain ends that hinder the molecular motions.

Matějka's group studied the effect of reactivity, structure and morphology on the thermo-mechanical properties of mono-functional reactive POSS-reinforced network with respect to its multi-functional reactive counterpart, based on DGEBA and a commercial hardener, Jeffamine D2000 [60-62]. They found that the POSS-POSS interaction is the main factor in determining the network structure which affects the resultant thermo-

mechanical properties. POSS-polymer chain interactions only play a minor role. The tendency to aggregate is much stronger for POSS pendant groups along the polymer backbone, and crystallization can occur. For cross-linked POSS, they only aggregate slightly at the junctions depending on reaction conditions. It is found that the thermal and thermo-mechanical properties of the epoxies with pendant POSS are better than the epoxies with cross-linked POSS at the network junctions, likely due to the crystalline domains acting as physical cross-link points. At high mass fractions of the mono-functional POSS ($> 70\%$), there is great topological constraint which decreases the chain motions, leading to additional reinforcing of the networks.

Kourkoutsaki *et al.* investigated the polymer dynamics of mono-functional reactive POSS/epoxy nanocomposites, and detected when mono-functional POSS are incorporated into the epoxy networks, there is an increase of free volume resulting from the loose packing of the epoxy chains disrupted by the bulky POSS cages [67].

Liu *et al.* demonstrated that as with the case of multi-functional reactive POSS discussed earlier, macro-phase separation caused by incorporation of the mono-functional POSS units can be avoided with the use of small molecule curing agents [63].

Zucchi *et al.* studied the effect of pre-reaction of the mono-functional reactive POSS on the morphology of the epoxy network and the crystallinity of the POSS domains [64]. They postulated that there is a certain extent of polymerization-induced phase separation occurring in all mono-functional reactive POSS networks, leading to inhomogeneity and large crystalline POSS domains. By pre-reacting POSS with the curing agent for a period of time, the solubility of the POSS is improved and the extent of polymerization-induced phase separation occurring will be much reduced. Thus, a more homogeneous network can be achieved.

2.5.3 Unbonded POSS as molecular silica

POSS functionalized with non-reactive groups can be incorporated into epoxy resins as molecular silica fillers by physical mixing. In this case, no chemical bonds are formed between the matrix and the POSS. The dispersion of the POSS fillers in the resins is determined by the interactions between the network and fillers [110]. The use of unbonded POSS in epoxies is not as widely studied as the covalently bonded POSS fillers, probably because of the difficulties in dispersing the fillers due to POSS propensity for aggregation [71-73].

In a bid to uniformly disperse the unbonded POSS in epoxies, Zheng's group have developed novel POSS cages with amphiphilic character [71-72]. By incorporating them into epoxy, it is found that various morphologies can arise depending on the amphiphilic POSS content. They attributed the effect to the POSS nano-structures being able to form *via* self assembly due to their amphiphilic character, where the hydrophobic cages come together and the hydrophilic end-capped 'tails' of the POSS extend out into the epoxy matrices, not unlike that of a micelle. Due to the amphiphilic nature of the end-capped POSS, they migrate and enrich the surface of the nanocomposites, imparting increased surface hydrophobicity and reduced surface free energy.

Wang *et al.* studied the effect of octa-vinyl POSS on the degradation behaviour and flame retardancy of epoxy resins containing phosphorous [73]. The thermogravimetric data shows the synergistic effect of the phosphorous-based epoxy with the unbonded POSS fillers. The phosphorous promotes char formation whereas the degraded POSS siliceous layer protects the char from thermal degradation. The POSS fillers also reduce the rate of heat released and the total heat evolved, demonstrating improved flame retardance.

2.6 Clay/epoxy Nanocomposites

Given the abundance and low cost of clay with the widespread use of epoxies, much work has been done on incorporating clay as nano-fillers into epoxies to improve their inherent thermal and thermo-mechanical properties [108]. The addition of clay generally increases the T_g of the epoxy systems, due to the hindrance of segmental polymer motions at the filler-matrix interfaces. However, some studies have shown that increasing the amount of clay content leads to reductions in T_g [111-114]. They are attributed to the plasticizing effect of the clay surfactant chains that increase the mobility of the cross-linked networks and the presence of un-reacted resin monomers caused by the screening effect of clay.

The thermo-mechanical properties of the epoxy systems also improve with the incorporation of clay. The enhancement of the modulus of the clay/epoxy nanocomposites can be ascribed to the high aspect ratio of the exfoliated clay platelets [108]. The reinforcement effect brought about by the shear deformation and stress transfer to the clay platelets is dependent on the extent of the intercalation/exfoliation i.e. how well the dispersion of clay is in epoxies. Recently, Ngo *et al.* have studied the effect of temperature, duration and speed of pre-mixing on the dispersion of Cloisite 30B clay in DGEBA epoxy [115]. Their findings show that pre-mixing at higher speed and temperatures improved the intercalation/exfoliation of clay during cure. The longer duration of pre-mixing is shown to allow better diffusion of the resin monomers into the clay inter-galleries so that during curing, better intercalation of the clay can be achieved. Longer pre-mixing also break down the clay into smaller aggregates for better dispersion.

The presence of clay is shown to have a positive effect on the reduction of the thermal coefficient of expansion (CTE) [113, 116]. The reduction is attributed to the interaction of

the rigid clay platelets that hinder the motion of the network junctions, impeding the expansion of the polymer chains at elevated temperatures.

2.7 Summary

The incorporation of POSS in epoxy nanocomposites and their resultant properties has been reviewed above. Inclusion of reactive POSS in amine-cured epoxies is shown to give improvements to the inherent thermal and thermo-mechanical properties of the hybrids. However, difference in cure kinetics between the reactive POSS fillers and matrix monomers has detrimental effects on the homogeneity and properties of the resultant networks. Mono-functional reactive POSS have also been investigated as potential clay intercalating agents in polymer nanocomposites. Large interlayer *d*-spacing of the POSS modified clays have been reported. Improvements in the thermal properties of the nanocomposites due to the presence of the POSS have also been reported. Some work has been done to disperse non-reactive functional POSS in epoxies by tailoring the molecular architecture of the POSS with amphiphilic character.

3 INFLUENCE OF CURE KINETICS ON PROPERTIES OF POSS-EPOXY CROSS-LINKED NETWORKS

POSS bearing reactive groups incorporated into amine-cured epoxies allow for the modification of the network structure and chemical composition that leads to improvements in the thermal and thermo-mechanical properties have been discussed previously in Chapter 2. Due to the dissimilar reactivities between the reactive POSS compounds and matrix monomers, the resultant kinetics difference between the individual resin components will affect the properties of the cured epoxy hybrids. Therefore, cure kinetics is expected to play a more pivotal role when reactive POSS compounds are incorporated in epoxy-anhydride networks. Thus, in order to establish the structure-property relationship in POSS modified epoxy-anhydride networks, it is essential to study the effect of cure kinetics of the POSS compounds with the resin monomers on the resultant properties of the cured hybrids.

In this study, we have prepared novel epoxy-based hybrid networks containing octakis(dimethylsiloxybutyl epoxide) octasilsesquioxane (OB) with hexahydrophthalic anhydride (HHPA) as the curing agent and 1H-imidazole as the catalyst [32]. *N,N,N',N'*-tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM), a widely used epoxy compound, was used as a co-monomer. Cure kinetics of the OB/HHPA and TGDDM/HHPA systems were studied. The progress of the cure reactions was monitored to elucidate the influence of the reactions on the thermal and thermo-mechanical properties of the resultant hybrid materials. The morphology of the hybrid resins was also investigated to correlate the homogeneity of the POSS dispersion to their resultant thermal properties. Dynamic kinetics analysis of POSS with different tether lengths, octakis(dimethylsiloxyglycidyl

epoxide) octasilsesquioxane (OG) and octakis(dimethylsiloxy epoxide) octasilsesquioxane (OE), was also conducted to investigate the tether length effect on the cure kinetics of the hybrid epoxy systems. Work done on reducing the kinetics difference between resin components by tailoring the tether chemistry of POSS to anhydride moieties is also reported.

3.1 Experimental

3.1.1 Materials

Starting POSS materials, octakis(dimethylsiloxy) octasilsesquioxane $T_8[\text{OSiMe}_2\text{H}]_8$, and octakis(vinyldimethylsiloxy) octasilsesquioxane $T_8[\text{OSiMe}_2\text{CH}=\text{CH}_2]_8$ were purchased from Hybrid Plastics Co. Acetic anhydride, 1,2-epoxy-5-hexene, allyl glycidyl ether (AGE), *m*-chloroperoxybenzoic acid (*m*-CPBA) and TGDDM (epoxide equivalent weight = 110-115 g/equiv.) were obtained from Sigma-Aldrich. Platinum divinyltetramethyldisiloxane complex, Pt (dvs) was purchased from Aldrich and diluted to a 2 mM solution in anhydrous toluene. HHPA ($\geq 95\%$) and 1H-imidazole were obtained from Fluka. Octa(aminophenyl) octasilsesquioxane (OAPS) was purchased from Mayaterials Inc. and further purified by reduction with ammonium formate and Pd/C. 5-(2,5-dioxotetrahydrofurfuryl)-3-methyl-3-cyclohexyl-1,2-dicarboxylic acid anhydride (EPICLON) was obtained from Merck Chemicals. All chemicals were used as received.

3.1.2 Synthesis of POSS-epoxy cross-linkers

OB and OG were synthesized according to the methods reported by He's group as shown in Scheme 3.1 [23]. OE was synthesized using Zhang's method with slight

modifications, the synthesis route given in Scheme 3.2 [80]. The structures and purities were verified by nuclear magnetic resonance (NMR), matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF-MS), Fourier transform infrared (FTIR) spectroscopy, size exclusion chromatography (SEC) and elemental analysis.

NMR and MALDI-TOF-MS experiments were conducted at the Institute of Materials Research and Engineering (IMRE), A*STAR, Singapore. ^1H , ^{13}C and ^{29}Si NMR spectra were recorded in deuterated chloroform (CDCl_3) at 25 °C on a Bruker AVANCE 400 NMR spectrometer at 400.13 MHz. IR spectra were obtained using a Perkin Elmer Instruments Spectrum GX FTIR spectrometer. The samples were cast on circular BaF_2 plates and spectra collected at an IR range from 700 to 4000 cm^{-1} at a resolution of 4 cm^{-1} . SEC analysis was carried out on an Agilent Technologies 1100 Series GPC analysis system calibrated with polystyrene standards and chloroform was used as the eluant at a flow rate of 1.0 mL/min. Elemental analysis was performed at the Department of Chemistry in National University of Singapore, Singapore.

OB In a 50 mL round bottomed flask equipped with a reflux condenser and a magnetic stirring rod, $\text{T}_8[\text{OSiMe}_2\text{H}]_8$ (2.5 g, 2.46 mmol) was dissolved in 5 mL of anhydrous toluene under dry N_2 environment. 8 equivalent of 1,2-epoxy-5-hexene (2.22 mL, 19.68 mmol) and a catalytic amount of Pt (dvs) catalyst (0.12 mL, 2mM) were added to the solution and the reaction mixture was heated to 60 °C. After completion of the exothermic reaction, the temperature was increased to 90 °C and stirred for 24 h. After removal of the excess 1,2-epoxy-5-hexene by rotary evaporation, the product was concentrated *in vacuo* at 40 °C to obtain a clear liquid. ^1H NMR (CDCl_3) (δ , ppm): 0.14 [$\text{Si}(\text{CH}_3)_2\text{CH}_2$], 0.63 ($\text{SiMe}_2\text{CH}_2\text{CH}_2$), 1.43-1.52 ($\text{SiMe}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ epoxy), 2.44 (CH_2 epoxy), 2.73-2.89 (CH epoxy). ^{13}C NMR (CDCl_3) (δ , ppm): -0.01 [$\text{Si}(\text{CH}_3)_2\text{CH}_2$],

17.8 (SiMe₂CH₂CH₂), 23.1 (SiMe₂CH₂CH₂CH₂), 29.8 (SiMe₂CH₂CH₂CH₂CH₂), 32.5 (SiMe₂CH₂CH₂CH₂CH₂ epoxy), 47.3 (CH epoxy), 52.4 (CH₂ epoxy). ²⁹Si NMR (CDCl₃) (δ, ppm): -100.4 (Si-O-Si), 20.9 (OSiMe₂). FTIR (KBr, cm⁻¹): 2946 (ν-CH), 1090, 770 (ν-Si-O-Si), 916 (δ-C-O), 846 (ν-C-O). MALDI-TOF-MS: Calcd. *M*_w 1803.1; Found 1801.7. C₆₄H₁₃₆O₂₈Si₁₆: Calcd. C, 42.67; H, 7.55. Found: C, 42.54; H, 7.29.

OG In a 50 mL round bottomed flask equipped with a reflux condenser and a magnetic stirring rod, T₈[OSiMe₂H]₈ (5.0 g, 4.92 mmol) was dissolved in 10 mL of anhydrous toluene under dry N₂ environment. 8 equivalent of AGE (4.68 mL, 39.36 mmol) and a catalytic amount of Pt (dvs) catalyst (0.24 mL, 2mM) were added to the solution and the reaction mixture was heated up to 50 °C. After completion of the exothermic reaction, the temperature was increased to 90 °C and stirred for 24 h. After removal of the excess AGE by rotary evaporation at 40 °C, the product was concentrated *in vacuo* at 40 °C to obtain a clear liquid. ¹H NMR (CDCl₃) (δ, ppm): 0.15 [Si(CH₃)₂CH₂], 0.59 (SiMe₂CH₂CH₂), 1.60 (SiMe₂CH₂CH₂CH₂O), 2.56-2.75 (CH₂ epoxy), 3.10 (CH epoxy), 3.40 (SiMe₂CH₂CH₂CH₂O), 3.33-3.66 (OCH₂ epoxy). ¹³C NMR (CDCl₃) (δ, ppm): 0.14 [Si(CH₃)₂CH₂], 14.1 (SiMe₂CH₂CH₂), 23.6 (SiMe₂CH₂CH₂CH₂O), 44.6 (SiMe₂CH₂CH₂CH₂O), 51.1 (OCH₂ epoxy), 71.8 (CH epoxy), 74.4 (CH₂ epoxy). ²⁹Si NMR (CDCl₃) (δ, ppm): -100.4 (Si-O-Si), 8.53 (OSiMe₂). FTIR (KBr, cm⁻¹): 2925 (ν-CH), ~1080 (ν-Si-O-Si), 906 (δ-C-O). SEC (polystyrene standards, CHCl₃ solvent): Calc. *M*_w = 1931 g/mol; Found *M*_n = 1644, *M*_w = 1913, PDI = 1.16.

Scheme 3.1. Hydrosilylation reaction routes for (a) OB; and (b) OG.

OE In a 50 mL round bottomed flask equipped with a reflux condenser and a magnetic stirring rod, $T_8[OSiMe_2CH=CH_2]_8$ (5.0 g, 4.08 mmol) and 10 equivalent of *m*-CPBA (7.04 g, 40.8 mmol) was dissolved in 40 mL of DCM under dry N_2 environment. The reaction mixture was refluxed at 50 °C and stirred for 5 hours. *m*-CBA was precipitated out as the reaction proceeded. The reaction flask was then cooled in ice to allow further precipitation of *m*-CBA which was then filtered off. The filtrate was neutralized with 0.1M sodium hydrogen carbonate solution before being washed twice with water and once with brine. The organic layer was then dried using anhydrous magnesium sulphate. The mixture was filtered and the DCM removed by rotary evaporation to obtain the crystalline white powder. 1H NMR ($CDCl_3$) (δ , ppm): 0.18-0.23 [$Si(CH_3)_2CH_2$], 2.21 (*CH* epoxy), 2.64-2.89 (*CH*₂ epoxy). ^{13}C NMR ($CDCl_3$) (δ , ppm): 0.20 [$Si(CH_3)_2CH_2$], 43.2 (*CH* epoxy), 44.6 (*CH*₂ epoxy). ^{29}Si NMR ($CDCl_3$) (δ , ppm): -100.7 (*Si-O-Si*), 8.57 (*OSiMe*₂). FTIR (KBr, cm^{-1}): 2960 (ν -CH), ~1080 (ν -*Si-O-Si*), 878

(*v*-C-O). SEC (polystyrene standards, CHCl₃ solvent): Calc. $M_w = 1350$ g/mol; Found $M_n = 1042$, $M_w = 1110$, PDI = 1.07.

Scheme 3.2. Epoxidation route for OE.

3.1.3 Preparation of the hybrid epoxy networks

The chemical structures of the compounds used in the preparation of the hybrid epoxy networks in this work are shown in Scheme 3.3. The compositions of the epoxy networks and the conditions for the cure are summarized in Table 3.1. The concentration of OB in the resins was defined according to the relationship below,

$$\text{OB conc. (mol.\%)} = \frac{\text{Number of moles of OB}}{\text{Number of moles of (OB + TGDDM)}} \times 100 \quad (3.1)$$

The catalyst concentration is defined as the molar ratio of 1H-imidazole/HHPA. The OB/TGDDM/HHPA resins were prepared by first pre-mixing OB and HHPA with the catalyst at 110 °C for a certain time period (Stage I) and then quenching the precursor in ice. Stoichiometric ratio of TGDDM was then mixed with the precursor homogeneously at room temperature. The mixture was degassed under vacuum at ~40 °C. It was then poured into an Al mould coated with a mould-releasing agent, cured in a Memmert air-

circulating convection oven at 140 °C and then post-cured in an inert-gas-purged oven at 200 °C (Stage II). TGDDM/HHPA and OB/HHPA resins were prepared accordingly but omitting Stage I.

Scheme 3.3. Chemical structures of (a) OB; (b) OG; (c) OE; (d) TGDDM; (e) HHPA; and (f) 1H-imidazole.

3.1.4 Cure kinetics

Dynamic cure kinetics was studied by differential scanning calorimetry (DSC) using a TA Instruments DSC 2010 in nitrogen atmosphere. TGDDM/HHPA, OB/HHPA and OG/HHPA mixtures with the catalyst concentration of 0.09 mol.% were prepared and ~5 mg each was sealed in a hermetic pan. The rate of reaction of the mixtures was monitored at an isothermal temperature of 140 °C until no further heat flow can be detected. The

mixtures were also heated at four different heating rates (5, 10, 15 and 20 °C/min) from 25 °C to 300 °C.

Table 3.1. Compositions and curing conditions for preparation of the hybrid networks.

Sample	OB conc. (mol.%)	OB conc. (wt.%)	Catalyst /HHPA molar ratio	Reaction Time		
				Stage I	Stage II (h)	
				at 110 °C (min)	First cure at 140 °C	Post-cure at 200 °C
TGDDM/HHPA	0	0.0	0.009	0	1	4, 24
5 mol.% OB-0	5	11.0	0.009	0	1	4, 24, 72
5 mol.% OB-10	5	11.0	0.009	10	1	24
5 mol.% OB-15	5	11.0	0.009	15	1	24
5 mol.% OB-20	5	11.0	0.009	20	1	24
5 mol.% OB-10-H	5	11.0	0.027	10	1	24
10 mol.% OB-10	10	20.0	0.009	10	1	24
OB/HHPA	100	74.5	0.009	0	1	24
OB/HHPA-H	100	74.5	0.09	0	1	24

3.1.5 Monitoring of Stage I reaction

DSC To simulate Stage I reaction, 5 mol.% OB and 0.009 mol.% 1H-imidazole were mixed with HHPA, and sealed in hermetic pans. Isothermal heating scans were recorded at 110 °C for 60 min using a TA Instruments DSC 2010 in nitrogen atmosphere.

FTIR The samples collected at different pre-mixing time were cast on circular BaF₂ plates, and the FTIR spectra were obtained using a Perkin Elmer Instruments

Spectrum GX FTIR spectrometer at room temperature from 700 to 4000 cm^{-1} . A total of 20 scans were recorded at a resolution of 4 cm^{-1} for averaging each spectrum.

SEC The samples collected at different pre-mixing time were dissolved in chloroform, and the SEC measurements were carried out using an Agilent Technologies 1100 Series GPC analysis system calibrated with polystyrene standards with chloroform as the eluant at a flow rate of 1.0 mL/min.

3.1.6 Synthesis of POSS-anhydride

The synthesis of the POSS-anhydride, OEpPOSS, was carried out by imidization reaction between OAPS and EPICLON using a method slightly modified from Krishnan *et al.* [85]. In a 250 mL 2-necked round bottomed flask equipped with a magnetic stirring rod, the cycloaliphatic dianhydride, EPICLON (9.16 g, 34.6 mmol) was dissolved in 130 mL of anhydrous DMF at room ambient under dry N_2 environment. OAPS (2.0 g, 1.73 mmol), pre-dissolved in 20 mL of anhydrous DMF, was added drop-wise into the reaction mixture which was then stirred at room ambient for 6 h. The formed amic acid was chemically imidized. A catalytic amount of triethyl amine was added (0.3 mL) and the reaction mixture was stirred well. Acetic anhydride (6.52 mL, 69.2 mmol) were then added drop-wise and the resultant mixture was stirred for 2 days under constant N_2 bubbling at room temperature. Ethyl acetate (600 mL) was added and the resulting solution was washed four times with water. The organic layer was dried with magnesium sulphate and filtered. The solvent was removed *via* rotary evaporation and the solid was washed with 1:4 (v/v) ethyl acetate/chloroform. The precipitate was filtered out and dried *in vacuo* at room ambient to yield a slightly yellow powder. FTIR (KBr, cm^{-1}): 1776 (*v*-

C=O imide out-of-phase), 1710 (ν -C=O imide in-phase), 1377 (ν -C-N imide), 1233 (ν -C-O-C anhydride), 1119 (ν -Si-O-Si).

3.1.7 Preparation of POSS-anhydride/epoxy hybrids

The 5, 10 and 15 mol.% POSS-anhydride hybrid resins were prepared by dissolving OEpPOSS in HHPA at a moderate temperature and the resultant mixture quenched in ice. TGDDM was then added and mixed with a high-speed mechanical stirrer to yield a clear homogeneous mixture. The mixture was degassed *in vacuo* at ~ 40 °C and cured for 1 h at 140 °C in an air-circulating oven and post-cured for 24 h at 200 °C in an inert-gas-purged oven. Their equivalent control samples (EPICLON/TGDDM/HHPA) were also prepared accordingly.

3.1.8 Characterization

Scanning Electron Microscopy (SEM) Morphology studies were carried out using a JEOL JSM 6340F field emission scanning electron microscope. The samples were fractured cryogenically using liquid nitrogen and the fractured surfaces were applied to the SEM measurements.

DSC T_g s were determined by a TA Instruments DSC 2010 under nitrogen purge from room ambient to 300 °C at a heating rate of 10 °C/min. The inflexion point of the transition region was taken to be the T_g s of the samples.

Thermogravimetric Analysis (TGA) The thermal stability of the cured resins were investigated by a TA Instruments High Resolution TGA 2950 thermogravimetric analyzer over a temperature range of 80 °C to 700 °C under nitrogen at a heating rate of 20 °C/min. The temperature at 5 % weight loss was taken as the thermal degradation temperature T_d .

Dynamic Mechanical Analysis (DMA) Storage moduli of the cured samples were recorded with a dynamic mechanical analyzer DMA Q800 from TA Instruments. The samples were polished to $\sim 17.5 \times 13.0 \times 3.0$ mm before being mounted on a single cantilever clamp and measured at a frequency of 1.0 Hz and a heating rate of 3 °C/min from 25 °C to 300 °C.

Thermo-mechanical Analysis (TMA) Coefficient of thermal expansion (CTE) measurements were conducted using a TA Instruments TMA 2940 thermo-mechanical analyzer at a heating rate of 3 °C/min from room ambient to 300 °C in a nitrogen atmosphere.

3.2 Results and Discussion

The POSS-epoxy modified epoxy-anhydride system, OB/TGDDM/HHPA, will be discussed in the following sections as the model system for the study of the effect of reaction kinetics on the properties of resultant anhydride-cured epoxy hybrids. The tether length effect on the cure kinetics was studied with the inclusion of OG/TGDDM/HHPA and OE/TGDDM/HHPA systems. The effect of POSS tether chemistry on the reaction kinetics will be discussed using OE_{ep}POSS as the model POSS-anhydride compound.

3.2.1 Effect of catalyst concentration

The cure profiles of OB/HHPA and TGDDM/HHPA are depicted in Fig. 3.1a and b, respectively. Without any catalyst, the cure peak temperature of OB/HHPA reached 400 °C (Curve I in Fig. 3.1a). Too high a cure temperature would result in excessive evaporation and decomposition of the reaction mixtures, thus a catalyst has to be added to help to bring the cure temperature to feasible values. With 1H-imidazole as the catalyst,

the cure peaks were shifted to much lower temperatures. The higher the catalyst concentration, the larger will be the shift (Fig. 3.1a).

Fig. 3.1. DSC thermograms of (a) OB/HHPA; and (b) TGDDM/HHPA with catalyst/HHPA molar ratio of 0 (I), 0.009 (II) and 0.09 (III).

The reaction mechanism of the anhydride with the epoxy is depicted in Scheme 3.4. It shows that the increased reactivity of the systems is brought about by the interactions of the amine site in 1H-imidazole with the anhydride and epoxide groups, which produce adducts containing highly reactive alkoxide ions to initiate the rapid anionic copolymerization, i.e. esterification, between epoxies and HHPA [96, 117]. It is worth noting that some alkoxide ions produced in the step 3 in Scheme 3.4 may not be able to react with HHPA due to the steric hindrance posed by the OB attached [18, 26]. A relatively high epoxy-anhydride ratio was thus used. The excess amount of epoxy may cause homo-polymerization, i.e. etherification between the epoxide groups, to some extent.

TGDDM was chosen as a co-monomer in this study because it has four short arms with reactive sites so that can potentially give high cross-linking density and hence

desirable properties. The addition of TGDDM into the reaction mixtures brings in however a reaction that is in competition with the one between OB and HHPA. Fig. 3.1b shows that the cure peak for TGDDM/HHPA was located at a much lower temperature, as compared to that of OB/HHPA, when no catalyst was used. This is due to the fact that there are internal catalytic sites (tertiary amine) in TGDDM to catalyze the anhydride ring opening [101]. With the catalyst, the cure peak temperatures of the TGDDM/HHPA system also reduced, but to a less extent as compared to the shifts for the OB/HHPA system. Thus, as the catalyst concentration increased, the cure peaks for OB/HHPA and TGDDM/HHPA became closer to each other.

Scheme 3.4. Schematic cure mechanism of catalyzed epoxy-anhydride system.

3.2.2 Cure kinetics

To compare the reaction rates of OB/HHPA and TGDDM/HHPA systems in the presence of the catalyst, isothermal DSC experiments were carried out at 140 °C for OB/HHPA and TGDDM/HHPA respectively, with the same catalyst concentration. The results are presented in Fig. 3.2. TGDDM apparently reacts with HHPA much faster than OB at this particular temperature. Isothermal DSC experiments conducted at 110 °C and 200 °C showed similar trends. However, they could not yield a proper conversion versus time curve as the reaction between OB and HHPA at 110 °C was too slow while the one between TGDDM and HHPA at 200 °C was too fast to be captured properly.

Fig. 3.2. (a) Isothermal DSC thermograms of TGDDM/HHPA and OB/HHPA systems at 140 °C; and (b) conversion as a function of time for TGDDM/HHPA and OB/HHPA systems derived from (a).

To further compare the reactivities of OB and TGDDM towards HHPA in the presence of the catalyst, dynamic kinetic analysis was performed using two established non-isothermal kinetic models: the Kissinger and Flynn-Wall-Ozawa models [103-105]. Fig. 3.3 shows the DSC thermograms and their respective Arrhenius plots from the

dynamic heating experiments conducted at rates between 5 and 20 °C/min. The two exotherm peaks are due to the etherification and esterification reactions as discussed earlier. By applying the Kissinger and Ozawa methods, the activation energies can be calculated from the slope of the Arrhenius plots.

Fig. 3.3. (a) Typical dynamic DSC thermograms; (b) and their respective Arrhenius plots obtained by Kissinger and Ozawa methods for the OB/HHPA system.

Table 3.2 summarizes the results obtained from the dynamic kinetics analysis. Linear relationships were obtained, confirming the validity of the models for the systems under study. The activation energies calculated based on the two models were in close agreement. The analysis shows that the OB/HHPA system has significantly higher activation energy than that of the TGDDM/HHPA system, entailing that the rate of the reaction between TGDDM and HHPA will increase faster with temperature than the one between OB and HHPA even with a relatively high concentration of the catalyst. From the isothermal and dynamic DSC analysis, we may derive that the reaction between TGDDM and HHPA is faster than that between OB and HHPA in the temperature range studied. Thus, it is highly likely that OB would not be incorporated well into the network if OB, TGDDM and HHPA were mixed together to react simultaneously.

Table 3.2. Peak exotherm temperatures (T) at different heating rates (q) and the corresponding activation energies (E_a) of the TGDDM/HHPA and OB/HHPA systems.

q (°C/min)	T (°C)	
	TGDDM/HHPA	OB/HHPA
5	115	129
10	127	141
15	135	148
20	142	154
E_a (kJ/mol)		
Kissinger	62.6	75.3
Ozawa	65.8	78.1

3.2.3 Effect of pre-mixing

In order for OB to be well connected to the network, it was allowed to react with HHPA first *via* pre-mixing (Stage I). TGDDM was then mixed with the precursors for further curing (Stage II). To investigate the effectiveness of Stage I reaction, DSC, FTIR and SEC techniques were used to monitor the progress of the reaction as a function of time. Fig. 3.4 displays a typical isothermal DSC thermogram of an OB/HHPA mixture with 5 mol.% OB (epoxide/anhydride molar ratio = 5/50) under simulated pre-mixing conditions. It was observed that the maximum reaction rate was reached at about 14 minutes before tapering off as time increased.

Fig. 3.4. Isothermal DSC thermogram of 5 mol.% OB/HHPA under the simulated pre-mixing condition, i.e. at 110 °C.

FTIR was used to follow the changes in the functional groups of the reaction mixture as the pre-mixing proceeded, as illustrated in Fig. 3.5. A strong symmetric Si-O-Si stretching peak at $\sim 1100\text{ cm}^{-1}$, typical of silsesquioxane cages [89], was present in all the spectra and was used as an internal reference. It can be observed that the asymmetric stretching C=O band of HHPA at $\sim 1898\text{--}1838\text{ cm}^{-1}$ decreased in intensity slightly while its corresponding symmetric stretching band at $\sim 1824\text{--}1742\text{ cm}^{-1}$ sharpened as the pre-mixing reaction proceeded [118]. The anhydride C=O groups were converted to the aliphatic C=O ester bonds due to the esterification reaction between HHPA and the oxirane groups of OB. This is evident from the growing aliphatic ester stretching band at $\sim 1745\text{--}1715\text{ cm}^{-1}$ [118]. A quantitative analysis of the conversion of the functional groups based on FTIR spectra is however not possible due to the overlapping of the bands.

Fig. 3.5. Evolution of the FTIR spectrum of 5 mol.% OB/HHPA during the pre-mixing reaction.

Fig. 3.6 shows the SEC chromatograms of the reaction mixture at various pre-mixing time. It can be seen that as the pre-mixing time increased, HHPA content in the mixture decreased, which signifies that the reaction between OB and HHPA has taken place. At the starting point (0 min), the mass distribution curve (inset in Fig. 3.6) already shows a broadening on the right side of the spectrum i.e. the higher molecular weight side, which implies that the reaction may have started before the system reached 110 °C. The increase in molecular weight at this stage is mainly due to the attachment of HHPA to OB since the fraction of the molecules with molecular weight higher than 3000, which is roughly the sum of the formula weights of one OB and eight HHPA molecules, is relatively small.

Fig. 3.6. Evolution of SEC chromatograms of a 5 mol.% OB/HHPA reaction mixture in Stage I; the inset is the mass distribution curves.

A small fraction of OB dimers may have been formed, as illustrated in Scheme 3.5. After 10 min of pre-mixing, a tail appears on the high molecular weight side. This signifies that reaction between HHPA and oxirane groups of OB have led to the formation of a significant amount of OB dimers and trimers. When the reaction mixture was quenched to room temperature, it remained as a low-viscosity liquid. As the pre-mixing time increased to 15 min, the tail extended more to the right with the major peak becoming narrower as more OB dimers, trimers and even oligomers have formed although the viscosity of the reaction mixture was still fairly low at room temperature due to the excess amount of HHPA. At 20 min, the viscosity became too high for homogeneity of the system to be maintained when TGDDM was added at room temperature.

Scheme 3.5. (a) OB oligomer formation as a function of pre-mixing time; and (b) the chemical structure of a dimer, i.e. two OB molecules attached to a HHPA molecule, formed in Stage I.

The morphology of the hybrids was examined using SEM. The micrographs are shown in Fig. 3.7. With no pre-mixing (A and D), some irregular-shaped white regions of $\sim 0.3\text{--}1.0\text{ }\mu\text{m}$ can be observed, which are likely to be POSS-rich domains. This may be caused by the higher rate of cure between the TGDDM-HHPA reaction pair, thus OB were excluded and aggregated together to form POSS-rich domains. With the inclusion of the pre-mixing step (B and E), sub-micron-sized particles can be observed but their population is very small. The particles are likely to be POSS-rich clusters, i.e. OB oligomers, formed during the pre-mixing. With prolonged pre-mixing time, i.e. 20 min (C and F), the population of the POSS-rich clusters increased, which implies that more OB oligomers were formed during the pre-mixing.

Fig. 3.7. SEM micrographs of the fractured surfaces of 5 mol.% OB hybrid materials with various pre-mixing times: 0 min (A and D), 10 min (B and E), 20 min (C and F).

Properties of the hybrids are strongly dependent on how well the POSS cages are incorporated into the networks. The dependence of the T_g of the hybrids on Stage I reaction becomes evident in Fig. 3.8. Without pre-mixing, the T_g achieved was much lower than that of the hybrid prepared *via* the two-stage cure. This can be attributed to the higher reactivity of the epoxide groups on TGDDM and the increasing steric hindrance during the curing process, which resulted in the absence of anhydride molecules around OB so that a large number of epoxide groups on OB were not bonded to the network till the end of the post-cure. The cross-linking density is thus not effectively boosted by the addition of OB, and the un-reacted flexible tethers may also act as plasticizers, permitting easier chain segmental movement. However, if the pre-mixing time was too long, the formation of OB oligomers will lower the concentration of functional groups available for cross-linking and some POSS tethers will also likely be left un-reacted due to steric

hindrance from oligomer formation. This reduced the overall cross-linking density, bringing about a significant reduction in T_g .

Fig. 3.8. DSC thermograms depicting T_g s of the hybrids containing 5 mol.% OB at different pre-mixing times. The resins were cured at 140 °C for 1 h and post-cured at 200 °C for 24 h.

3.2.4 Effect of post-cure time

Due to the relatively low reactivity of OB compared to TGDDM, post-cure was necessary to improve the overall properties of the resins. To prevent the thermal oxidative degradation of the anhydride-cured resins, post-cure was carried out in argon for different time periods. It was found that T_g increased with the post-cure time, as depicted in Fig. 3.9, due to the increase in the cross-linking density. However, it was found that with prolonged post-cure time i.e. 72 h, the epoxy resins yielded poorer thermo-mechanical properties. This suggested that thermal degradation of the epoxy resin may have taken place, albeit slower than in air. Hence, post-cure time was limited to 24 h for our further studies on properties.

Fig. 3.9. (a) DSC thermograms depicting T_g s of the hybrids containing 5 mol.% OB (pre-mixing time = 10 min) at different post-cure times. (b) T_g s of the hybrids as a function of post-cure time.

3.2.5 Thermal properties

Table 3.3 summarizes the thermal properties of the hybrid networks. OB/HHPA shows very poor thermal properties, except its T_d , due to the presence of a large amount of flexible chains, and the molecular geometry and low reactivity of OB, which leave a large amount of flexible organic tethers unbonded to the network. The increase in the catalyst concentration by ten times (OB/HHPA-H) improved the properties only slightly. The T_d improved for all OB-modified networks. The T_d is obviously dependent on the OB concentration, suggesting that the amount of the inorganic POSS cages in the resins influences the thermal stability of the resins significantly.

A large jump of ~ 20 °C in T_g , as compared to TGDDM/HHPA, was observed with the addition of 5 mol.% OB, which is equivalent to 11 wt.% OB, into the resin (5 mol.% OB-10). The increase was mainly due to the high cross-linking density resulted from the bonding of the organic tethers of OB onto the network. In contrast to T_d , when the OB

loading was increased to 10 mol.% (10 mol.% OB-10), T_g dropped with the same premixing and cure conditions. The high functionality of OB can produce an increase in cross-linking density and hence T_g , while the flexibility of the organic arms on OB can lead to a decrease in T_g . These two counteracting effects justify the presence of a maximum in T_g as a function of OB loading. In addition, the lower T_g for 10 mol.% OB-10 may also be caused by the increased probability of the formation of OB oligomers during the pre-mixing when the amount of OB molecules per unit volume was higher. With a higher catalyst concentration (5 mol.% OB-10-H), T_g was improved further due to the increase in the degree of conversion, which was however accompanied by a decrease in the homogeneity of the resin, as discussed below.

Table 3.3. Summary of thermal and thermo-mechanical properties of the epoxy hybrids.

Sample	T_g (°C)	T_d (°C)	E' (GPa)			CTE ($\mu\text{m}/\text{m } ^\circ\text{C}$)	
						30-50	50-100
			50 °C	100 °C	220 °C	°C	°C
TGDDM/HHPA	166	337	2.5±0.02	2.3±0.01	0.05±0.00	62	70
5 mol.% OB-10	184	344	2.6±0.06	2.3±0.02	0.10±0.02	68	78
5 mol.% OB-10-H	188	342	2.3±0.03	1.9±0.12	0.11±0.03	61	71
10 mol.% OB-10	180	354	2.1±0.01	1.7±0.02	0.09±0.00	69	87
OB/HHPA	-	379	0.3±0.03	0.1±0.02	0.13±0.01	146	191
OB/HHPA-H	-	378	1.1±0.05	0.4±0.08	0.30±0.01	267	260

Dynamic mechanical analyses showed that the glassy moduli E' of the hybrid with 5 mol.% OB increased slightly at 50 °C, as compared to TGDDM/HHPA. The increase may

be attributed to the incorporation of the rigid POSS cages. However, for the hybrid with 10 mol.% OB cured under the same conditions (10 mol.% OB-10), the glassy E' decreased by a significant amount, as compared to that of 5 mol.% OB-10. A plausible explanation may be increased inhomogeneity in the POSS distribution as more OB oligomers were formed during the pre-mixing stage, evident in Fig. 3.10 where larger micron-sized POSS domains are observed in the 10 mol.% OB-10 resin. The doubling of POSS content increased the likelihood for formation of large POSS agglomerates, leading to poorer POSS distribution compared to the 5 mol.% OB-10 resin.

Fig. 3.10. SEM micrographs of the fractured surfaces of (A) 5, and (B) 10 mol.% OB-10 hybrid networks.

The increase in the catalyst concentration led to an increase in the cross-linking density as evidenced by the higher rubbery E' of 5 mol.% OB-10-H (curve c in Fig. 3.11) than that of 5 mol.% OB-10 (curve b in Fig. 3.11). The glassy E' was however decreased due to the inhomogeneity of the resin caused by the very fast curing of TGDDM during the pre-mixing and the first cure at 140 °C. It can also be observed that the OB/HHPA networks (e and f) showed a significantly higher rubbery modulus than the rest of the

resins due to the high cross-linking density resulting from the high POSS fractions in the resins. However, the presence of large amount of flexible organic tethers leads to much lower T_g s (below room temperature).

Fig. 3.11. Storage modulus E' as a function of temperature for (a) TGDDA/HHPA; (b) 5 mol.% OB-10; (c) 5 mol.% OB-10-H; (d) 10 mol.% OB-10; (e) OB/HHPA; (f) OB/HHPA-H.

The TMA measurements indicate that with the addition of OB, the CTE values of the hybrids were slightly higher than that of TGDDM/HHPA. He *et al.* suggested that the increased CTE was due to the flexible organic tethers forming a large amount of soft interphase around the POSS cages in the resins [119]. In the present case, this can also be attributed to the incomplete cure of the organic tethers on OB.

3.2.6 Effect of POSS tether length on cure kinetics

By tailoring the organic tether architecture, more rigid POSS can be deployed to enhance the stiffness of the epoxy networks and improve the global properties. However,

increase in structural rigidity of POSS will have a bearing on the cure kinetics. To investigate this relationship, three types of POSS with differing tether lengths in increasing rigidity, OG<OB<<OE have been prepared (See Scheme 3.3).

Table 3.4. Peak exotherm temperatures (T) at different heating rates (q) and the corresponding activation energies (E_a) of the OB/HHPA and OG/HHPA systems.

q (°C/min)	T (°C)	
	OB/HHPA	OG/HHPA
5	129	127
10	141	140
15	148	148
20	154	155
E_a (kJ/mol)		
Kissinger	75.3	63.0
Ozawa	78.1	66.2

Table 3.4 presents the results obtained from the dynamic kinetics analysis for the OG/HHPA and OB/HHPA systems. The analysis shows that the OG/HHPA system has a much lower E_a i.e. higher rate of reaction than the OB/HHPA system. It may be attributed to the longer and more flexible OG tethers that are able to react easier with the surrounding HHPA molecules due to the lowering of steric hindrance caused by the nano-sized POSS cage i.e. higher degree of freedom (Scheme 3.6). The poorer kinetics exhibited by OB/HHPA system reflects that the shorter and more rigid OB tethers increases the steric hindrance for reaction with HHPA molecules. The dynamic kinetics of OE/HHPA system is not shown as the solubility is very poor for stoichiometric ratio of

OE in HHPA. However, as the OE tethers are even shorter, much poorer kinetics is expected as steric hindrance increases.

Scheme 3.6. Interaction between POSS of different tether lengths with HHPA molecules.

Therefore, as the length of POSS tethers decreases i.e. higher rigidity, the degree of freedom reduces. The probability of the POSS interacting with HHPA monomers during copolymerization will likely be lowered, resulting in an increase in the amount of un-reacted POSS tethers in the network which will be detrimental to the thermal properties of the epoxy hybrids, as evident in Table 3.5.

The 5 mol.% OB-10 hybrid shows a drop in the T_g over the 5 mol.% OG-10 hybrid, plausibly due to the higher amount of the un-reacted tethers in the network. It may be attributed to increase in steric hindrance, leading to lower reactivity between OB and HHPA molecules, as discussed above. Correspondingly, the glassy E' of 5 mol.% OB-10 decreased, which can be ascribed to the un-reacted OB cubes acting as ‘internal plasticizers’, facilitating network deformation. The T_g of 5 mol.% OE-10 hybrid is the lowest since OE has the highest steric hindrance to reaction with the base monomers due to its short and rigid tethers. Similarly, albeit the higher glassy E' over the 5 mol.% OB-

10 network due to the short and stiff tethers of OE, the glassy E' was lower compared to the 5 mol.% OG-10 network. This plausibly indicates the presence of even higher amount of un-reacted tethers in the network, further implied by a low rubbery E' at 200 °C which is an indication of the amount of cross-linking density in the network.

Table 3.5. Summary of thermal properties of the hybrids with different POSS tether length. The hybrids were cured for 1 h at 140 °C in air and post-cured for 72 h at 200 °C in argon.

Sample	T_g (°C)	E' (GPa)			
		50 °C	100 °C	150 °C	200 °C
5 mol.% OG-10	194	2.4	2.2	2.0	0.2
5 mol.% OB-10	191	2.2	1.9	1.6	0.2
5 mol.% OE-10	188	2.4	2.1	1.8	0.1

3.2.7 Anhydride-functionalized POSS hybrids

In the earlier sections, it is observed that the cure kinetics difference between the two reaction pairs i.e. POSS-epoxy/HHPA and TGDDM/HHPA is large due to the self-catalytic effect of TGDDM which leads to incomplete cure and inhomogeneity in the epoxy networks. To minimize the kinetics difference, an attempt was made to functionalize POSS with reactive anhydride groups (Scheme 3.7). In this way, the reactivity between the epoxy monomers and non-POSS monomers will be reduced. As the anhydride groups do not homo-polymerize, better dispersion of the POSS may also be achieved, improving the network homogeneity.

Scheme 3.7. Idealized synthesis route for the POSS-anhydride, OEpPOSS.

To lessen the likelihood of dimers (OAPS-EPICLON-OAPS) and oligomers formation, EPICLON was added in excess (~ 2.5 times the stoichiometric ratio of OAPS). The components in the reaction mixture have similar solubilities, thus mixed solvents were employed to remove as much excess starting material as possible. However, it is not possible to isolate the OEpPOSS in its entirety. Hence, the structure of OEpPOSS was not able to be fully elucidated by common characterization methods. The characteristic bands of OEpPOSS depicted in the FTIR spectra in Fig. 3.12 at 1119, 1233, 1377, 1710 and 1776 cm^{-1} assigned to the Si-O-Si stretching vibration, C-O-C anhydride, imide C-N, and carbonyl (C=O in-phase and out-of-phase) respectively indicate that amic acid have been cyclized to form OEpPOSS, although it cannot be concluded that all tethers were successfully functionalized.

Fig. 3.12. FTIR spectra of (a) OEPOSS; and (b) OAPS.

Hence, control samples containing corresponding concentrations of EPICLON are prepared to illustrate the effect of the POSS-anhydride on the properties of the hybrid resins. Table 3.6 summarizes the thermal properties data for the POSS-anhydride hybrids. No significant improvement in T_g s can be observed at all POSS concentrations compared to the control resins. It may be attributed to competing factors i.e. the multi-functional POSS-anhydride increased the amount of chemical cross-link junctions that hinder the segmental chain motion but simultaneously, the bulky POSS cages can also act as plasticizers, facilitating chain motion. The glassy E' of the POSS-anhydride hybrids is generally improved as compared to the control resins. In fact, unlike POSS-epoxy hybrids discussed earlier, POSS-anhydride hybrids exhibit improved E' with increased POSS loadings. A plausible reason may be the smaller kinetics difference between resin components, leading to improved cure and homogeneity, which is apparent in Fig. 3.13 where relatively homogeneous morphologies have been observed containing few visible sub-micron POSS agglomerates ($\sim 0.1 \mu\text{m}$) with increasing POSS-anhydride content.

Fig. 3.13. SEM micrographs of hybrids with increasing POSS-anhydride content: (A) 5; (B) 10; and (C) 15 mol.% OEPOSS.

Table 3.6. Summary of thermal and thermo-mechanical properties of the POSS-anhydride epoxy hybrids.

Sample	T_g (°C)	E' (GPa)			CTE ($\mu\text{m/m } ^\circ\text{C}$)	
		50 °C	100 °C	150 °C	30-100 °C	100-150 °C
5 mol.% EPICLON*	216	2.6±0.04	2.4±0.05	2.2±0.06	60.2±1.6	69.5±3.7
5 mol.% OEPOSS	214	2.7±0.19	2.4±0.07	2.1±0.08	59.0±2.4	68.2±3.4
10 mol.% EPICLON*	224	2.5±0.07	2.3±0.02	2.1±0.01	58.7±2.8	67.6±2.9
10 mol.% OEPOSS	223	2.5±0.08	2.4±0.05	2.2±0.03	57.8±1.0	64.8±2.0
15 mol.% EPICLON*	215	2.7±0.19	2.5±0.18	2.2±0.17	59.6±1.4	66.3±3.5
15 mol.% OEPOSS	216	3.2±0.03	2.9±0.04	2.6±0.07	55.4±1.7	63.5±1.8

*control resin.

In the earlier case, the kinetics difference between POSS-epoxy/HHPA and TGDDM/HHPA is large. Changing the POSS tether to anhydride removed the kinetics difference between the competing epoxy reaction pairs; however there is still some, albeit small kinetics difference between the TGDDM/POSS-anhydride and TGDDM/HHPA reaction pairs due to the difference in the steric hindrance caused by anhydride groups on OEpPOSS and HHPA for TGDDM molecules. TMA measurements also indicate generally lower CTEs. This is likely due to the reduction in amount of soft interphase around the POSS cages as the organic tethers are comprised of rigid aromatic rings coupled with similarly rigid imide linkages.

3.2.8 Summary

In summary, a new class of POSS-epoxy hybrid networks cured with an anhydride has been prepared using a two-stage cure method. As evidenced from the kinetics data, OB has lower reactivity than TGDDM; hence a pre-mixing reaction was necessary to enhance bonding of the OB tethers to the networks for improved properties. SEM studies have shown that pre-mixing helps to improve the homogeneity of the resins. By introducing 5 mol.% OB into the networks, the hybrid prepared *via* the optimized two-stage reactions displayed a large jump of ~ 20 °C in T_g , which was accompanied by slight improvements in T_d and E' , while CTE was increased slightly, as compared to TGDDM/HHPA. The increased OB loading of 10 mol.% in the hybrids caused the global properties to reduce, which can be ascribed to the incomplete cure of the networks and the formation of large OB oligomers that de-homogenizes the networks. Dynamic kinetics analysis reveals that the shorter tether length of POSS, the slower the kinetics, possibly due to steric hindrance during reaction. By changing the tether to an anhydride, the cure

kinetics difference is lowered, as evident by the improvements in thermal and thermo-mechanical properties of the OEpPOSS/epoxy hybrids.

4 CATALYTIC AND REINFORCING EFFECTS OF POSS-IMIDAZOLIUM SURFACTANTS IN EPOXY AND CLAY/EPOXY SYSTEMS

As seen in Chapter 3, cure kinetics play a major role in determining the properties of the cured epoxy hybrids when POSS units with multiple reactive groups are incorporated in the networks. Large kinetics difference between the POSS compounds and the matrix monomers will result in large amounts of un-reacted POSS tethers. By introducing mono-functional POSS compounds bearing a single reactive group, the cure kinetics problem may be mitigated to a certain extent, yet provide nano-reinforcement effect by covalent bonding to the epoxy networks as pendent POSS which are reviewed in Chapter 2.

By functionalizing the mono-functional POSS with suitable organic surfactants, it can also be used to improve the compatibility of clay with epoxies. As seen in Chapter 2, the attractiveness of this approach resides in the large interlayer *d*-spacing brought about by the bulky POSS cages which may help to improve clay intercalation in the epoxy matrices, and the potential to impart synergistic effects of POSS and clay on resin property improvements.

Mono-functional POSS functionalized with imidazolium moiety discussed in Chapter 2 is seen to be an attractive proposition as besides the large basal *d*-spacing exhibited by the bi-layer packing of the POSS-imidazolium in clay interlayer, the thermal and thermo-oxidative resistances of the corresponding modified clays are higher than the POSS-ammonium modified clays owing to the higher thermal stability of imidazolium moiety [120]. Furthermore, imidazolium salts are well known latent catalysts, decomposing at elevated temperatures to imidazole moieties that can initiate the cure of anhydride-based

epoxies [99]. Thus, the presence of POSS-imidazolium modified clays in epoxy-anhydride systems may allow cure reactions to be initialized in clay galleries, which may facilitate clay dispersion and influence the properties of the resultant nanocomposites positively.

In this study, we prepared novel anhydride-cured epoxy hybrids containing POSS-imidazolium (POSS-IMC) and POSS-imidazolium modified MMT (POSS-MMT). We demonstrate the catalytic effect of the POSS-imidazolium, and correlate the morphologies of the resultant hybrids to their thermal and thermo-mechanical properties.

4.1 Experimental

4.1.1 Materials

Pristine montmorillonite clay (Na-MMT) with CEC of 145 mmol/100 g was obtained from Nanocor Inc. Chlorobenzyl isobutyl-POSS was purchased from Hybrid Plastics Ltd. USA. 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate (ECHM) and 1,2-dimethylimidazole were purchased from Sigma-Aldrich. HHPA ($\geq 95\%$) was bought from Fluka. All chemicals were used as received.

4.1.2 Synthesis of POSS-imidazolium surfactant

The POSS-imidazolium surfactant, 1,2-dimethyl-3-(benzyl heptaisobutyl POSS) imidazolium chloride (POSS-IMC), was synthesized according to the method reported by Toh *et al.* [12]. The structure was verified by proton NMR experiment conducted at IMRE, A*STAR, Singapore, and FTIR spectroscopy. In a round bottom flask equipped with a reflux condenser and a magnetic stirring rod, chlorobenzyl isobutyl-POSS (10.0 g,

10.6 mmol) and 1,2-dimethylimidazole (1.33 g, 13.8 mmol) were dissolved in 30 mL of dry tetrahydrofuran at 80 °C and the reaction mixture was refluxed for 3 days. Upon the completion of the exothermic reaction, the solvent was removed by rotary evaporation and the crude product was re-crystallized by precipitation with ethyl acetate. The product was filtered and washed with acetonitrile, and dried *in vacuo* at 40 °C overnight to yield a white solid. ¹H NMR (CDCl₃) (δ, ppm): 0.61-0.63 (m, 14H), 0.92-0.96 (m, 42H), 1.81-1.90 (m, 7H), 2.75 (s, 3H), 3.97 (s, 3H), 5.51 (s, 2H), 7.27 (d, 2H, *J* = 7.9 Hz), 7.43 (d, 1H, *J* = 6.3 Hz), 7.55 (d, 1H, *J* = 5.0 Hz), 7.68 (d, 2H, *J* = 7.5 Hz). FTIR (KBr, cm⁻¹): 1100 (ν-Si-O-Si), 1538-1589 (ν-imidazolium ring).

4.1.3 Modification of MMT clay

POSS-imidazolium modified clay, denoted as POSS-MMT, was also prepared using a slightly modified procedure reported in ref. 12. The feed loading of POSS-IMC used was 120 mol.% of the CEC of Na-MMT. Pristine clay was weighed into a beaker containing distilled water and vigorously stirred for 20 h at room temperature. The resultant clay slurry was further homogenized at 6000 rpm for 20 min and stored for 2 days before being gently poured into a 1 L round bottom flask, discarding the sedimentation at the bottom. POSS-IMC, pre-dissolved in ethanol, was then slowly added to the clay slurry under vigorous agitation and the mixture was stirred at 80 °C for 3 days. The clay slurry was subjected to centrifugal extraction to obtain the modified clay which was then washed with ethanol several times until no chloride ions were detected by 0.1N AgNO₃ solution. The modified clay was further washed with 5:4 (v/v) hot tetrahydrofuran/water *via* Soxhlet extraction overnight and then dried *in vacuo* at room temperature for 2 days before being pulverized into fine powder of size ~80 μm.

4.1.4 Preparation of the epoxy hybrid resins

The amount of POSS-MMT to be added into the resins was calculated by using thermogravimetric methods and the proposed formula in ref. 12,

$$A\left(\frac{X}{100}\right) + B\left(1 - \frac{X}{100}\right) = C \Rightarrow X = \left(\frac{C - B}{A - B}\right) \times 100 \quad (4.1)$$

where X (%) is the organic weight loss of POSS-MMT, A (%) is the char residue of POSS-IMC, B (%) is the char residue of Na-MMT and C (%) is the char residue of POSS-MMT taking into consideration the hydrolysis of pristine clay (4.87 wt.%). The concentration of POSS-MMT in the resins was defined according to a relationship below,

$$\text{MMT conc. (wt.\%)} = \frac{\text{Weight of MMT (Y, g)}}{\text{Weight of [(ECHM + HHPA + MMT(Y)) (g)]}} \times 100 \quad (4.2)$$

$$\text{POSS - MMT (Z) (g)} = \left[\frac{Y \text{ (g)}}{(100 - X) / 100} \right] \quad (4.3)$$

Replacing Y with Z in Eq. 4.2 will give the percentage weight concentration of POSS-MMT in the epoxy resin.

The chemical structures of the compounds used in the preparation of the hybrids are presented in Scheme 4.1. POSS-MMT was added in small portions to ECHM under high-speed mechanical stirring and the mixture was continuously pre-mixed at 50 °C for 20 h, after which 0.8 stoichiometric equivalent of HHPA was added into the mixture. It was then stirred at 110 °C for 1 h before degassing under vacuum, after which the mixture was

poured into Al moulds and cured at 140 °C for 2 h in a Memmert air-circulating oven and post-cured at 200 °C for 24 h in Ar environment. The hybrid obtained is denoted as H-POSS-MMT. Corresponding neat epoxy resin, denoted as ECHM/HHPA, and an ECHM/HHPA/POSS-IMC hybrid with similar POSS-imidazolium content to that of H-POSS-MMT, denoted as H-POSS-IMC, were prepared accordingly without the pre-mixing step, using only high-speed mechanical stirring. For preparing H-POSS-IMC, a small amount of tetrahydrofuran was also added in the mixing stage to aid POSS-IMC dispersion. The resin compositions are summarized in Table 4.1.

Scheme 4.1. Structures of (a) POSS-IMC; (b) POSS-MMT; (c) ECHM; and (d) HHPA.

4.1.5 Cure kinetics

Dynamic cure kinetics studies were carried out on ECHM/HHPA and ECHM/HHPA/POSS-IMC mixtures using differential scanning calorimetry with a TA Instruments DSC 2010. The samples (~5 mg) were prepared in hermetically sealed Al

pans and heated at four different heating rates (5, 10, 15 and 20 °C/min) from room ambient to 300 °C in a nitrogen-purged environment. Cure profiling studies on ECHM/HHPA, ECHM/HHPA/POSS-IMC and ECHM/HHPA/POSS-MMT mixtures were also performed accordingly at a heating rate of 10 °C/min.

Table 4.1. Compositions and cure conditions of H-POSS-IMC and H-POSS-MMT networks.

Sample	MMT content (wt.%)	POSS-imidazolium content (wt.%)
ECHM/HHPA	0.0	0.0
H-POSS-IMC	0.0	1.4
H-POSS-MMT	1.0*	1.3*

*Calculated from the wt.% of POSS-imidazolium in POSS-MMT determined using TGA.

4.1.6 Characterization

TGA The POSS-imidazolium content in POSS-MMT was estimated from the degradation residues of Na-MMT, POSS-IMC and POSS-MMT measured with a TA Instruments TGA 2950 thermogravimetric analyzer over a temperature range of 100 °C to 800 °C in air, at a heating rate of 10 °C/min.

FTIR The FTIR spectra were obtained using a Perkin Elmer Instruments Spectrum GX FTIR spectrometer at room temperature from 700 to 4000 cm⁻¹. A total of 50 scans were recorded at a resolution of 2 cm⁻¹ for averaging each spectrum. Three samples were prepared for FTIR measurements. An ECHM/HHPA/POSS-IMC blend was prepared by mixing ~20 wt.% POSS-IMC with ECHM/HHPA at 110 °C for 1 h and the paste was cast onto circular BaF₂ plates. The blend was cured and POSS-IMC powder

annealed at 140 °C for 2 h, respectively, and they were ground and mixed with KBr and compressed into pellet form.

POM To examine the dispersion state of clay in the pre-mixing process, the ECHM/POSS-MMT mixtures taken at pre-determined intervals were coated on glass slides and images were captured on a Nikon BW-H501 polarizing optical microscope equipped with Media Cybernetics Image-Pro Express imaging software.

SEM Morphological studies were carried out using a JEOL JSM 7600F field emission scanning electron microscope. The samples were fractured cryogenically with liquid nitrogen and the fractured surfaces applied to SEM measurements.

Transmission Electron Microscopy (TEM) TEM samples were cut using a Leica Ultracut microtome equipped with a diamond knife and collected on 400 mesh carbon-coated copper grids. They were analyzed with a JEOL 2010 transmission electron microscope at an accelerating voltage of 200 kV.

WAXS Wide angle X-ray scattering profiles were recorded in a Siemens D5005 X-ray diffractometer using Cu K α_1 radiation at 40 kV and 40 mA at a scan range from $2\theta = 1.5^\circ$ to 30° .

Modulated DSC T_g s were determined by a TA Instruments DSC 2920 modulated DSC at a heating rate of 3 °C/min at modulating amplitude of ± 0.48 °C over a period of 60 s. The inflexion point of the transition region was taken to be the T_g s of the samples.

DMA See Section 3.1.8 for thermo-mechanical property measurements.

TMA See Section 3.1.8 for CTE measurements.

4.2 Results and Discussion

4.2.1 Catalytic effects of POSS-IMC and POSS-MMT

Imidazolium quaternary salts are well known latent catalysts for initiation of the polymerization of epoxies. At elevated temperatures with trace moisture, they are able to decompose to form active imidazole moieties that initiate the ring opening reaction of the monomers, thereby lowering the cure temperatures. It is plausible that POSS-IMC may display similar catalytic effect, given the imidazolium group tethered at one corner of the POSS cage.

To confirm this effect, dynamic kinetics analysis was carried out on the ECHM/HHPA system, one without any catalyst and the other with 1.4 wt.% POSS-IMC, *via* DSC at four different heating rates. The activation energies (E_a s) are calculated from the slopes of the ensuing Arrhenius plots shown in Fig. 4.1 using two established non-isothermal models i.e. the Kissinger and Flynn-Wall-Ozawa models [103-105]. Linear relationships were obtained; hence the two models were validated.

Fig. 4.1. Dynamic DSC thermograms and their respective Arrhenius plots for the ECHM/HHPA (A and B); and ECHM/HHPA/POSS-IMC systems (C and D).

Table 4.2 summarizes the results obtained from the kinetics analysis. The analysis indicates that the ECHM/HHPA/POSS-IMC system has much lower activation energy than that of the neat ECHM/HHPA, entailing that the addition of POSS-IMC is able to initiate the ring opening reactions of the monomers at significantly lower temperatures.

Table 4.2. Peak exotherm temperatures (T) at different heating rates (q) and the corresponding activation energies (E_a) of the ECHM/HHPA and ECHM/HHPA/POSS-IMC systems.

q (°C/min)	T (°C)	
	ECHM/HHPA	ECHM/HHPA/POSS-IMC
5	217	150
10	237	166
15	245	175
20	256	184
E_a (kJ/mol)		
Kissinger	69.7	59.1
Ozawa	74.3	63.1

The catalytic effect of POSS-IMC may be explained using the reaction mechanism depicted in Scheme 4.2. At elevated temperatures, trace amounts of water in the system undergo autoprotolysis. The dissociated OH^- anions attack and thermally cleave the N-C bond of the POSS-imidazolium cations to expose the active amine sites on the resultant imidazole moieties to the monomers, as shown in step 1 [120]. The increased reactivity of the system is brought about by the reaction of these amine sites with the epoxide and anhydride groups, yielding adducts containing highly reactive alkoxide and carboxylate ions to initiate rapid anionic copolymerization between the ECHM and HHPA molecules [117]. The consequence of this is that some POSS cages are covalently attached at chain ends, which may influence the relaxation behaviour of the networks, as will be discussed later.

Scheme 4.2. The proposed catalytic mechanism of the POSS-imidazolium for epoxy-anhydride system.

To support the proposed mechanism, FTIR spectra of the ECHM/HHPA/POSS-IMC blend, the corresponding cured resin and annealed POSS-IMC powder are compared in Fig. 4.2. For POSS-IMC (curve a), the two absorption bands at $\sim 1538\text{ cm}^{-1}$ and $\sim 1589\text{ cm}^{-1}$ can be assigned to the in-plane ring vibrations of the imidazolium moiety as reported by Petrak *et al.* [100]. The bands can also be observed in the FTIR spectrum of the ECHM/HHPA/POSS-IMC mixed at $110\text{ }^{\circ}\text{C}$ (curve b). However, for the resin cured at $140\text{ }^{\circ}\text{C}$ (curve c), the band at lower frequency is diminished whereas the other band becomes more prominent. The difference is not due to cure-induced crystallization of

POSS-IMC as the annealed POSS-IMC powder is also highly crystalline. The difference may thus be attributed to the change in local geometry of the ring. The substitution of the methyl group, which is nearly a free rotor, by a polymer chain may hinder the in-plane vibration of the ring and cause a subtle change in vibration frequencies.

Fig. 4.2. FTIR spectra of (a) POSS-IMC; (b) ECHM/HHPA/POSS-IMC mixture; and (c) its resultant resin. The peak intensities are not adjusted for clarity.

Fig. 4.3 shows the cure profiles of ECHM/HHPA, ECHM/HHPA/POSS-IMC and ECHM/HHPA/POSS-MMT at heating rates of 10 °C/min. Shoulder peak exotherms are seen at lower temperatures for all resin mixtures, possibly due to carboxylic acid impurities from HHPA. Comparing curve a with curve b, it is clear that the peak exotherm temperature is reduced from 237 °C for ECHM/HHPA to 166 °C for ECHM/HHPA/POSS-IMC, which corroborates with the activation energy values reported earlier. The peak exotherm temperature of ECHM/HHPA/POSS-MMT (curve c) is likewise lower than that of the neat ECHM/HHPA. This strongly suggests that the POSS-

imidazolium in MMT exhibits similar catalyzing effect as the POSS-IMC. However, with the same POSS-imidazolium content, the magnitude of E_a reduction brought about by POSS-MMT is smaller than that by POSS-IMC as implied by a smaller shift of the peak exotherm to the left for the ECHM/HHPA/POSS-MMT system. The weaker catalyzing effect of POSS-imidazolium in MMT may be due to the shielding effect of the clay platelets. Furthermore, POSS-imidazolium cations are ionically bonded to the clay layers so that their molecular motions are restricted as compared with the free POSS-IMC. Owing to the steric hindrance, a lower catalytic reactivity is expected.

Fig. 4.3. DSC thermograms of (a) ECHM/HHPA; (b) ECHM/HHPA/POSS-IMC; and (c) ECHM/HHPA/POSS-MMT mixtures at a heating rate of 10 °C/min.

4.2.2 Morphological studies

To investigate how the catalytic effects of POSS-IMC and POSS-MMT influence the properties of the resultant hybrids, it is essential to examine the dispersion states of nano-fillers in the hybrids. The H-POSS-IMC resin was visually transparent, indicating that

POSS-IMC was dispersed in ECHM/HHPA reasonably well at microscopic level. However, although the POSS-IMC content in H-POSS-IMC was only 1.4 wt.%, the resin exhibits a weak diffraction peak at $2\theta = 8.4^\circ$ (curve b in Fig. 4.4). The WAXS pattern of POSS-IMC shows a strong, sharp diffraction peak at the same position (curve a in Fig. 4.4), which is approximately the size of an isobutyl-substituted POSS cage and hence can be attributed to the intermolecular distance in POSS-IMC crystals. It indicates that POSS-IMC are able to aggregate and crystallize in H-POSS-IMC to some extent. SEM analysis on the fractured surfaces of H-POSS-IMC reveals the presence of sub-micron-sized irregular POSS-IMC aggregates (Fig. 4.5).

Fig. 4.4. WAXS patterns of (a) POSS-IMC; (b) H-POSS-IMC; (c) Na-MMT; (d) POSS-MMT; and (e) H-POSS-MMT. The intensity of the curves is not adjusted for clarity.

Fig. 4.5. SEM micrographs of the fractured surfaces of H-POSS-IMC showing irregular shaped POSS domains (white regions) at low (A) and high (B) magnifications.

Further analysis of H-POSS-IMC under TEM (Fig. 4.6) reveals the existence of domains of aggregated POSS crystals (A and B) as well as nano-sized crystalline (C) and amorphous (D and E) POSS aggregates. This indicates a possible occurrence of polymerization-induced phase separation that arises from the poor compatibility between POSS-IMC and ECHM/HHPA, and also the propensity of the POSS to aggregate [58, 60, 64]. It is important to note that some of these mono-reactive fillers participated in network formation and formed pendent POSS at the polymer chain ends so that the aggregation probably occurred in the pre-cure stage before the network formation. Both reacted and un-reacted POSS could aggregate and then took part in crystallization upon cooling, leading to crystalline as well as amorphous aggregates, as illustrated by the schematic in Fig. 4.7. The formation of such POSS aggregates influences the properties of the hybrid resin, as will be discussed in the next section.

Fig. 4.6. TEM micrographs (A to E) of H-POSS-IMC resin.

Fig. 4.7. Schematic illustrating POSS-IMC aggregation states in H-POSS-IMC resin.

For POSS-MMT, the POSS-imidazolium cations were incorporated into clay using the cationic exchange procedure before mixing with the epoxy. The mixture was pre-mixed under high-speed mechanical shear for an extended period to allow diffusion of epoxy molecules into the clay galleries [115]. The pre-mixing stage was monitored with

POM at selected intervals and the consequential micrographs suggest marked improvement in dispersion with prolonged mixing time and the clay was broken down into smaller particles gradually (Fig. 4.8). The resultant hybrids appeared to be homogeneous yet translucent, implying some degree of incompatibility between POSS-MMT and the matrix. As reported previously [12], the POSS-imidazolium cations are arranged in a disordered bi-layer packing structure within the clay galleries, hence the large basal d -spacing of 3.68 nm is detected in the WAXS pattern (curve d in Fig. 4.4). Owing to the catalyzing effect of the POSS-imidazolium cations, the co-polymerization may readily occur in clay galleries, resulting in an increase of the basal d -spacing to 3.77 nm (curve e in Fig. 4.4).

Fig. 4.8. Polarized optical micrographs of POSS-MMT pre-mixed with ECHM at 50 °C for 0 h (A); 8 h (B); and 20 h (C).

The TEM micrographs for the H-POSS-MMT resin are presented in Fig. 4.9 (A to C). The clay exhibits small tactoid (~5-10 clay layers) morphology, implying that most of the clay galleries have been intercalated (A and B) with some exfoliation (C). However, microscopic inhomogeneity is detected, as shown by random and homogenous dispersion of the clay stacks at some regions (B) but poor dispersion in other regions (A); the latter resulting in sub-micron-sized intercalated clay aggregates. A possible reason may be the

inhomogeneous packing of the POSS-imidazolium cations in POSS-MMT. The silsesquioxane cages are packed in a disordered bi-layer structure as illustrated in Scheme 4.1. This resulted in very strong POSS-POSS attraction forces in some regions. These attraction forces are weaker in disordered regions with lower packing density, resulting in larger d -spacings. This allows more resin molecules to diffuse into the clay galleries. Hence, at cure temperatures, these regions are able to intercalate/exfoliate easily. In contrast, more ordered regions with high packing density resulted in stronger POSS-POSS attraction forces, reducing the d -spacing of the clay galleries i.e. more tightly packed, hence the clay stacks are not able to exfoliate effectively. The consequence will be the uneven intercalation/exfoliation of the clay stacks, resulting in inhomogeneous dispersion of the clay in the network.

Fig. 4.9. TEM micrographs (A to C) of H-POSS-MMT resin.

An interesting dissimilarity is also observed between the morphologies of the two hybrids. Crystalline POSS aggregates were seen in the H-POSS-IMC resin (Fig. 4.6B). Despite having a similar amount of POSS-imidazolium in the clay, no POSS crystals can be detected, either in the epoxy matrix or within the clay galleries of the POSS-MMT resin (Fig. 4.9). One plausible explanation could be that the external shear forces

produced during the mixing of the resin was not large enough to dislodge the POSS-imidazolium, thus during curing, a substantial amount still remained attracted to the negatively charged clay platelets. Propensity for aggregation was negated since they were ionically bonded to clay and hence unable to aggregate and crystallize effectively during the network formation.

Fig. 4.10. Schematic illustrating the clay intercalation states in H-POSS-MMT resin.

Direct evidence is provided with closer scrutiny of the TEM micrograph (Fig. 4.9C), revealing that some POSS-imidazolium cations remain as a bi-layer structure (a faint line between two dark clay lines shown by arrow 1) or as a mono-layer (arrow 2) on the clay platelets. This however does not preclude the fact that some POSS-imidazolium cations may have reacted and became pendent POSS which could strongly interact with the POSS units attached on clay (Fig. 4.10). The effect of POSS interactions and divergent resin morphologies will have implications on the resultant thermal and thermo-mechanical properties of the hybrid.

4.2.3 Thermo-mechanical and thermal properties

Fig. 4.11. (A) Storage moduli E' and (B) loss moduli E'' as functions of temperature for (a) ECHM/HHPA; (b) H-POSS-IMC; and (c) H-POSS-MMT. Magnified rubbery moduli E' curves are shown in the inset in (A).

Fig. 4.11 depicts the storage moduli E' and loss moduli E'' of the neat and hybrid resins as functions of temperature. Thermal and thermo-mechanical properties of these materials are summarized in Table 4.3. From Fig. 4.11A, it can be observed that H-POSS-IMC (curve b) exhibits a slightly higher glassy E' over the neat resin (curve a) at temperatures above 100 °C. Based on the morphological model proposed above (Fig. 4.7), this is due to the formation of the POSS domains that leads to strong interactions among the pendent POSS units in the network. These rigid domains act as physical cross-link points in the network, providing nano-reinforcing effect by hindering polymer chain motion. The reinforcement effect can also be observed from the E'' curves plotted in Fig. 4.11B. For ECHM/HHPA (curve a), there is a broad shoulder peak before the T_g relaxation peak probably owing to the relaxation of the flexible ether (C-O-C) linkages formed by homo-polymerization of ECHM. These flexible aliphatic segments tend to

relax at lower temperatures before polyester segments start to relax. The physical cross-linking points help to retard the relaxation of these flexible segments, thus no shoulder E'' peak is seen for H-POSS-IMC (curve b).

From the inset in Fig. 4.11A, it is observed that there is a slight reduction in the rubbery E' of the H-POSS-IMC resin (curve b) in comparison with that of the neat resin (curve a). The rubbery E' is directly related to the cross-linking density of the network. Thus, the drop indicates a lower chemical cross-linking density of the H-POSS-IMC, which strongly supports the notion that a significant amount of POSS units are tethered at the ends of the polymer chains.

Table 4.3. Summary of thermal and thermo-mechanical properties of the neat and hybrid resins.

Sample	T_g (°C)	E' (GPa)			CTE ($\mu\text{m}/\text{m } ^\circ\text{C}$)	
		50 °C	100 °C	150 °C	30-50 °C	50-100 °C
ECHM/HHPA	215	2.6	2.3	2.0	74.0±3.5	81.0±3.1
H-POSS-IMC	205	2.6	2.4	2.2	68.5±2.1	72.3±3.5
H-POSS-MMT	197	3.1	2.8	2.4	69.9±2.7	79.5±3.3

This observation correlates with Fig. 4.11B where in the glass transition region, the E'' peak of H-POSS-IMC (curve b) has significantly higher amplitude than that of the neat epoxy (curve a), signifying a higher degree of chain relaxations in H-POSS-IMC at T_g . The pendent POSS units are tethered at the ends of polymer chains in H-POSS-IMC, lowering the number of chemical cross-link junctions in the network, while the strong interactions between pendent POSS units led to the formation of physical cross-link points that overrides the loss in chemical cross-link junctions. However, at T_g , the motion

of the polymer chain segments may destroy most nano-sized POSS domains in H-POSS-IMC, resulting in a higher degree of chain relaxations. Apart from lowering the number of chemical cross-link junctions, the pendent POSS units may also increase the overall free volume within the network owing to the relatively poor compatibility between the isobutyl POSS and the matrix. They collectively have a detrimental effect on the T_g of the H-POSS-IMC resin as given in Table 4.3.

The H-POSS-MMT resin (curve c in Fig. 4.11A) shows a marked improvement (~20 %) in the glassy E' over the neat resin owing to the reinforcement effect of the intercalated clay stacks dispersed in the network. Considering that only 1 wt.% of MMT is present in the H-POSS-MMT, the stress transfer between the matrix and clay might be fairly effective. Based on the morphological model proposed in Fig. 4.10, the stress transfer probably benefits from the relatively strong interactions between the pendent POSS units in the network and the POSS units attached on the MMT layers. Although the glassy E' is improved, owing to the heterogeneous morphology of the H-POSS-MMT, there are localized relaxations of the C-O-C chain segments in regions where the clay stacks are poorly dispersed, as shown by the shoulder appearing before the main E'' peak (curve c in Fig. 4.11B).

Cross-linking density of the H-POSS-MMT network was also reduced as compared with that of the neat epoxy as illustrated by the increase in amplitude of the E'' peak and lower rubbery E' of H-POSS-MMT (inset curve c). The lower cross-linking density of H-POSS-MMT is likely due to the high aspect ratios of the clay stacks that physically block the joining of the chains at the two sides of clay stacks. The T_g is also notably reduced by the incorporation of POSS-MMT. Inhomogeneous distribution of the clay stacks within the resin; lower cross-linking density and free volume increase caused by incompatibility are some of the main factors that may have contributed to the significant drop in T_g .

The CTE data shown in Table 4.3 indicates that there are reductions in CTE for both H-POSS-IMC and H-POSS-MMT in comparison with that of the neat resin. H-POSS-IMC exhibits the lowest CTE values as the POSS domains were able to restraint polymer network expansion. H-POSS-MMT displays smaller CTE reduction probably due to the poor dispersion of the clay layers in some regions. It is worthwhile to note that the constraint brought about by POSS-IMC domains faded away slowly with increasing temperature since a significant amount of POSS domains are crystalline in nature.

4.2.4 Summary

The findings reveal the synergistic qualities of the POSS-imidazolium surfactants. The cure studies suggest that both the free and clay-bonded POSS-imidazolium surfactants performed catalytic function, and can thus be used to tailor the cure of epoxy-anhydride systems. Furthermore, free POSS-IMC molecules and pendant POSS groups form sub-micron- and nano-sized domains in H-POSS-IMC, which act as physical cross-link points, provide the reinforcing effect by restricting chain motions in the glassy state. The incorporation of POSS-imidazolium in clay further enhances the reinforcing effect, i.e. gives rise to a ~20 % increase in glassy modulus with only 2.3 wt.% POSS-imidazolium modified clay, which is due to the high aspect ratio of clay and probably also the effective stress transfer from the matrix to the clay layers that originates from the strong interactions between the pendent POSS on the network and the bonded POSS on the clay.

5 INTERACTIONS OF UNBONDED POSS ON FILLER DISPERSION AND THERMAL PROPERTIES OF EPOXY NETWORKS

As seen in Chapters 3 and 4, with reactive groups, POSS compounds often undergo self-aggregation in competition with their chemical bonding to epoxy resins so that the dispersion state is highly influenced by cure kinetics. With non-reactive groups on POSS, their self-aggregation is in competition with their molecular dispersion in polymers. Thus, for epoxy resins with non-reactive POSS compounds, the compatibility between the organic groups of the POSS and epoxy networks becomes the dominant factor controlling the dispersion of the POSS. Furthermore, given their small molecular size, the incorporation of non-reactive POSS into epoxies may create extremely large interfacial areas and thus the interfacial interactions may significantly influence the properties of the hybrids.

POSS functionalized with phenyl groups such as octa-phenyl POSS (OPS) make an excellent subject for study as non-reactive functional POSS filler. The rigid phenyl groups may provide enhanced stiffness to the epoxy hybrids. As reviewed in Chapter 2, polar characteristics can be easily imparted to the predominantly hydrophobic non-polar POSS when functionalized with polar groups to study the change in the compatibility.

In this study, we prepared novel epoxy-anhydride hybrids containing octa-phenyl POSS (OPS) and brominated OPS as non-reactive functional nano-fillers. The reason to choose bromination is that the reaction can be controlled easily to achieve different levels of bromination, thus providing a good model system. The morphologies of the hybrids are correlated to the compatibility between the POSS and the epoxy resin. The surface

properties were studied using static contact angle measurements and XPS. The effects of interfacial interactions on thermal properties of the hybrid resins are also studied.

5.1 Experimental

5.1.1 Materials

TGDDM (epoxide equivalent weight = 110-115 g/equiv.) was purchased from Sigma-Aldrich. HHPA ($\geq 95\%$) was supplied by Fluka. OPS and octa(bromophenyl) octasilsesquioxane (OBPS) were obtained from Mayaterials Inc. Elemental bromine and iodine was bought from EMD Chemicals Inc. TGDDM, HHPA, OPS and OBPS were all used as received.

5.1.2 Synthesis of the unbonded POSS fillers

Brominated OPS with an average of 1 bromine atom per molecule (OPS-Br) and 13 bromine atoms per molecule (OPS-13Br) were synthesized using a modified method reported by He's group [86].

OPS-Br In a 500 mL round bottom flask equipped with a magnetic stirring rod, 4 equivalent of elemental bromine (0.60 mL, 11.64 mmol) was added drop-wise to a mixture containing OPS (3.0 g, 2.91 mmol) and anhydrous ferric chloride (0.12 g, 0.74 mmol) in 250 mL of dichloromethane at room temperature under vigorous stirring. After stirring at room ambient for 72 h, the solution was washed repeatedly with saturated sodium hydrogen carbonate solution to remove the excess bromine. The majority of the solvent was removed *via* rotary evaporation and the product was precipitated in large

amounts of ethanol. The precipitated product was then filtered and dried *in vacuo* at ~40 °C to yield an off-white powdery solid.

OPS-13Br In a 500 mL round bottom flask equipped with a magnetic stirring rod, 14 equivalent of elemental bromine (2.10 mL, 40.74 mmol) was added drop-wise to a mixture containing OPS (3.0 g, 2.91 mmol) and anhydrous ferric chloride (0.39 g, 2.41 mmol) and elemental iodine (0.18 g, 0.71 mmol) in 250 mL of dichloromethane at room temperature under vigorous stirring. After stirring at room ambient for 5 days, the solution was washed repeatedly with saturated sodium hydrogen carbonate solution to remove the excess bromine. The product was concentrated to ~20 mL *via* rotary evaporation and precipitated in large amounts of ethanol. The precipitated product was then filtered and dried *in vacuo* at ~40 °C to yield a white powdery solid.

The structures of OPS-Br, OPS-13Br and OBPS were verified by MALDI-TOF-MS conducted at IMRE, A*STAR, Singapore. As the bromination of OPS yielded mixtures of product, M_w peaks with the highest intensity in the MALDI-TOF-MS spectra are taken to be the average M_w of the brominated compounds (Fig. 5.1). MALDI-TOF-MS: OPS-Br = Calcd. M_w 1112.4; Found 1111.3. OPS-13Br = Calcd. M_w 2059.2; Found 2058.1. OBPS = Calcd. M_w 1664.7; Found 1663.6.

Fig. 5.1. MALDI-TOF-MS spectra of (a) OPS-Br; (b) OPS-13Br; and (c) OBPS with Ag^+ matrix.

5.1.3 Preparation of POSS-filled epoxy hybrids

The chemical structures of the compounds used are given in Scheme 5.1.

Scheme 5.1. Chemical structures of (a) OPS; (b) OPS-Br; (c) OBPS; (d) OPS-13Br; (e) TGDDM; and (f) HHPA.

The unbonded POSS-filled epoxy hybrids containing 5 wt.% OPS, OPS-Br, OBPS and OPS-13Br were prepared by first mixing the nano-fillers with HHPA at a moderate temperature, aided by ultrasound treatment. 1.2 stoichiometric equivalent of TGDDM was then added and mixed with a high-speed mechanical stirrer at room temperature. The mixture was then degassed *in vacuo* at ~40 °C and poured into Al moulds. The curing

took place in a Memmert air-circulating oven at 140 °C for 1 h and then post-cured in an inert-gas-purged oven at 200 °C for 24 h. The control resin (TGDDM/HHPA) was prepared accordingly.

5.1.4 Calculation of solubility parameters

The Hildebrand solubility parameters provide a numerical estimate of the degree of interaction between the components in the mixture. Similar values indicate the components are likely to be miscible in each other i.e. good compatibility. The Hildebrand parameters can be calculated by taking the square root of the summation of cohesive energy densities obtained from chemical group contributions of the component using the relationship shown below [121],

$$\delta = (U/V)^{1/2} = \left(- \sum U / \sum V \right)^{1/2} \quad (5.1)$$

where δ is the Hildebrand solubility parameter, U is the group molar vaporization energy and V is the group molar volume. The advantage of this method is that it requires knowledge of only the chemical structure of the components. Table 5.1 shows the group contributions of TGDDM, HHPA, OPS, and OBPS used in the calculation of Hildebrand parameters.

Table 5.1. Molar vaporization energies (U) and molar volumes (V) of the chemical groups [121].

Chemical group	U (kJ mol ⁻¹)	V (cm ³ mol ⁻¹)
6-membered ring	1.05	16.0
Conjugated double bonds	1.67	-2.2
—CH=	4.31	13.5
>C=	4.31	-5.5
—Br	12.39	30.0
—C ₂ O ₃ — (anhydride)	30.60	30.0
3-membered rings	3.14	18.0
—CH ₂ —	4.94	16.1
>N—	4.20	-9.0
>CH—	3.43	-1.0
—O—	3.35	3.8

5.1.5 Characterization

WAXS The samples were scanned with a Bruker AXS GADDS X-ray diffractometer using a Cu K α_1 X-ray source at an operational voltage and current of 40 kV and 40 mA respectively. The data was collected at 2 θ ranging from 1.5° to 30°.

SEM See Section 3.1.8 for SEM measurements.

TEM See Section 4.1.6 for TEM measurements.

Contact angle and free energy measurements The flat free surfaces of the hybrid resins were used for the static contact angle measurements with ultrapure water and

ethylene glycol as probe liquids. They were conducted with First Ten Ångströms FTA200 contact angle analyzer at room temperature. All samples were dried overnight at room ambient in the vacuum oven. The data was averaged over three replicated tests. The free surface energies of the samples were calculated according to the geometric mean model used by Ni and Zheng [71].

$$\cos \theta = \frac{2}{\gamma_L} \left[(\gamma_L^d \gamma_s^d)^{1/2} + (\gamma_L^p \gamma_s^p)^{1/2} \right] - 1 \quad (5.2)$$

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (5.3)$$

where θ is the contact angle, γ_L is the liquid surface tension with γ_L^d and γ_L^p being its dispersive and polar components respectively. H₂O: $\gamma_L = 72.80 \text{ mN m}^{-1}$, $\gamma_L^d = 21.80 \text{ mN m}^{-1}$, $\gamma_L^p = 51.00 \text{ mN m}^{-1}$. Ethylene glycol: $\gamma_L = 48.30 \text{ mN m}^{-1}$, $\gamma_L^d = 29.30 \text{ mN m}^{-1}$, $\gamma_L^p = 19.00 \text{ mN m}^{-1}$ [122].

X-ray Photoelectron Spectroscopy (XPS) The XPS data were acquired with VG ESCALAB 220I-XL X-ray photo-spectrometer at room ambient using an Al K α_1 X-ray source.

TGA Thermal and thermo-oxidative degradation of the cured resins were evaluated using a TA Instruments High Resolution TGA 2950 thermogravimetric analyzer over a temperature range of 100 °C to 800 °C in nitrogen and air environments respectively, at a heating rate of 20 °C/min. The char yield was taken at 700 °C.

DMA See Section 3.1.8 for thermo-mechanical property measurements.

DSC See Section 3.1.8 for T_g measurements.

TMA See Section 3.1.8 for CTE measurements.

5.2 Results and Discussion

5.2.1 Solubility of unbonded POSS in epoxy

The POSS cube is considered to be the smallest silica particles that can be produced today. The diagonal diameter of common octa-functional POSS compounds is typically less than two nanometres, which makes their mono-dispersion in polymer matrices by physical means a very challenging task due to the large contribution of interfacial energy to the enthalpy. Compatibility between the matrices and POSS compounds thus becomes extremely important as it dictates how well-dispersed the latter will be within the matrices.

Table 5.2. Calculated Hildebrand parameters of the individual resin components.

Resin component	Hildebrand solubility parameter, δ (MPa ^{1/2})
TGDDM	22.3
HHPA	23.6
OPS	21.1
OBPS	23.2

Table 5.2 presents the calculated Hildebrand solubility parameters of the individual components under study. As TGDDM and HHPA have similar δ values i.e. good compatibility, they are miscible in each other and form a single-phase epoxy resin when cured. However, there is a large difference in the δ values between OPS molecules and neat TGDDM/HHPA, thus poor solubility of OPS in the epoxy resin is expected. It can be observed that when polar bromo groups are attached to OPS molecules i.e. OBPS, the discrepancy in δ values between them and the epoxy matrix is reduced. This signifies increased compatibility, thus higher solubility between the brominated OPS molecules

with the matrix, plausibly due to increased polar interactions between them and the largely polar epoxy-anhydride matrix.

5.2.2 Morphologies of the unbonded POSS hybrids

Fig. 5.2 displays the WAXS patterns of the POSS and their corresponding hybrid resins. It can be seen that OPS exhibits many diffraction peaks portraying the structure typical of crystalline POSS. For OBPS, randomly substituted bromo groups disrupt the ordered packing of the compound, which results in an amorphous structure. The hump at $2\theta = \sim 2^\circ$ may be a part of the small-angle scattering profile from silsesquioxane cages that are randomly dispersed in the organic substituents.

The extent of the dispersion of the nano-fillers in the epoxy resin can be gleaned from the WAXS patterns of the hybrid resins. The WAXS pattern of the 5 wt.% OPS resin shows a similar amorphous halo to that of the neat TGDDM/HHPA resin but some weak diffraction peaks from crystalline OPS can still be observed. In addition, a sharp peak can be found at the $2\theta = 8.2^\circ$ (d -spacing of 1.08 nm) which can be attributed to the average inter-particle distance between the POSS cages in the OPS agglomerates. With an average of one bromo group attached to OPS, the diffraction peaks from crystalline POSS almost disappeared and the intensity of the 8.2° peak was also reduced, indicating improved dispersion of the POSS. No low-angle peak can be observed for 5 wt.% OBPS, implying that near nano-scale dispersion has been achieved. The broad peak at $2\theta = 22.6^\circ$ is likely to be associated with internal structures of individual OBPS molecule. When more bromo groups are attached to OPS i.e. 5 wt.% OPS-13Br, the WAXS pattern displays the similar amorphous halo to that of the neat TGDDM/HHPA resin, no peaks associated with crystalline POSS can be observed.

Fig. 5.2. WAXS patterns of the POSS fillers and their corresponding hybrids.

The SEM micrographs in Fig. 5.3 depict the morphologies of the fractured surfaces of the POSS-filled epoxy hybrids. As predicted earlier, with 5 wt.% OPS (A and B), numerous irregular POSS-rich regions (in white) of several microns in diameter can be observed. This can be ascribed to the non-polar nature of the organic groups on OPS, which makes it incompatible with the more polar epoxy-anhydride matrix. Thus, OPS molecules tend to agglomerate, leading to their poor dispersion in the resin. With the attachment of bromo groups to the phenyl rings of OPS, the compatibility between the POSS and matrix is improved, evident from the SEM micrographs of 5 wt.% OPS-Br (C and D). The number and size of POSS-rich domains are slightly decreased.

Fig. 5.3. SEM micrographs of fractured surfaces of unbonded POSS hybrids with 5 wt.% OPS (A and B); OPS-Br (C and D); OBPS (E and F); OPS-13Br (G and H).

When the average number of bromo groups per POSS cage is increased to eight (E and F), the POSS-rich regions have mostly disappeared. It shows that a further increase in

the compatibility between the POSS and the matrix brought by attaching more bromine atoms have led to a low tendency for agglomeration. When the number of bromine atoms per cage is increased further in the case of the 5 wt.% OPS-13Br (G and H), the POSS domains have virtually disappeared, implying that nano-scale dispersion of the POSS in the resin have been achieved. However, few sub-micron-sized POSS aggregates can still be observed.

Fig. 5.4. TEM micrographs of 5 wt.% OPS-13Br (A to D).

TEM analysis of the 5 wt.% OPS-13Br resin (Fig. 5.4) shows the presence of irregular POSS aggregates in the nano-sized dimensions. This may be attributed to the unbonded

POSS propensity for aggregation [60]. The POSS-POSS attraction forces are stronger than that of the weaker polar interactions between OPS-13Br molecules and the matrix monomers. During the pre-cure stage, the OPS-13Br molecules which do not take part in the network formation are able to come together to form amorphous POSS aggregates depicted in Fig. 5.4 (C and D) which shows the ‘growth’ of the POSS agglomerates in a ‘sea’ of well-dispersed POSS fillers.

5.2.3 Thermal properties

For non-reactive POSS fillers, the filler-matrix interactions and interfacial area are two key factors that influence the thermal properties of the POSS/epoxy networks. As depicted in Fig. 5.5, the 5 wt.% OPS resin exhibits a slightly lower T_g compared to the control resin. This may be attributed to the poor compatibility between OPS and the matrix which results in weak interfacial interaction. These weak interactions are easily diminished as temperature increases. The unbonded OPS fillers thus act as plasticizers, facilitating polymer chain motions at the filler-matrix interface at a slightly lower temperature. By attaching bromo groups onto OPS, its compatibility with the matrix improved, resulting in enhanced filler dispersion and interaction at the filler-matrix interface due to the strong polar interaction forces between them and the polar groups of the matrix. However, the polar forces brought by bromo groups fade away as the temperature increases. In the case of the epoxy resin filled with slightly brominated OPS (5 wt.% OPS-Br), the relatively weak polar forces brought by a small amount of polar bromo groups fades away quickly as the temperature rises, coupled with the increased interfacial free volume brought about by the attachment of the bromo groups, leads to a much lower T_g . As more bromo groups are tethered onto OPS (5 wt.% OBPS and OPS-

13Br), the interfacial area becomes extremely large but the improved dispersion of the POSS fillers results in much enhanced interfacial interaction i.e. large increase in the amount of polar attraction forces at the filler-matrix interface, thereby increasing the T_g of the resin over the 5 wt.% OPS-Br resin.

Fig. 5.5. DSC thermograms showing the T_g s of (a) TGDDM/HPA; (b) 5 wt.% OPS; (c) 5 wt.% OPS-Br; (d) 5 wt.% OBPS; and (e) 5 wt.% OPS-13Br resins.

The storage moduli E' curves for the various epoxy hybrids are illustrated in Fig. 5.6a. It is observed that with the addition of the unbonded POSS fillers, there are no significant improvements in the E' values over the control resin. In fact, lower E' values were obtained for the 5 wt.% OPS and OBPS hybrids. In the case of 5 wt.% OPS resin, incompatibility between the POSS fillers and the epoxy matrix result in poor dispersion and interfacial interactions which leads to an increase in the overall free volume of the resin. This caused the fillers to be ineffective in impeding deformation. In contrast, the 5 wt.% OPS-Br resin is shown to have only a slightly lower E' than the control resin, possibly due to a slight increase in aspect ratio or specific surface area of the fillers. It

contains a mixture of OPS-Br and OPS-2Br compounds which have slightly higher aspect ratio differences than OPS because of their irregular molecular shapes shown in Fig. 5.7. This results in higher specific surface area of the fillers, coupled by an increase in the polar interactions due to the attachment of bromo groups, leads to an improvement in E' over the 5 wt.% OPS hybrid.

Fig. 5.6. (a) Storage moduli E' and (b) loss moduli E'' as functions of temperature for the unbonded POSS hybrid resins.

The low glassy E' of the 5 wt.% OBPS resin may be caused by the extremely large interfacial volume resulting from the reasonably well-dispersed POSS cages. Since the spherical fillers have virtually no aspect ratio difference, coupled by the weak interactions that could be easily overcome by external stresses, deformation of the resin is promoted. Conversely, the 5 wt.% OPS-13Br resin is seen to exhibit higher glassy E' over the 5 wt.% OBPS resin. In fact, the glassy E' is shown to be slightly higher over the control resin. This is probably due to the increase in the surface area of the POSS nano-fillers coupled with a ~60 % increase in the amount of bromo groups that may have contributed to a significant enhancement of the filler-matrix interactions in the resin.

Fig. 5.7. 3-dimensional molecular models of (a) OPS-Br; and (b) OPS-2Br nano-fillers in 5 wt.% OPS-Br hybrid using CS Chem3D with MM2 energy minimization. The lengths are estimated from the diagonal apexes of the molecules.

The 5 wt.% OPS-Br and OPS-13Br hybrids portray higher amplitude E'' peaks than the control resin as shown in Fig. 5.6b, signifying higher degree of chain relaxations at T_g . This suggests that the dispersion of irregular-shaped particles with higher aspect ratio or high specific surface area may have enhanced the plasticizing effect, facilitating chain relaxation at the interface. Cross-linking density is also reduced, probably due to the particle hindrance during formation of the network. Conversely, the 5 wt.% OPS and OBPS resins show similar E'' peaks with the control resin, indicating that the cross-linking density is not affected by the spherical POSS particles.

The CTE data shown in Table 5.3 indicates that the hybrids do not exhibit any significant improvement over the control resin. With POSS loading, slightly lower CTEs are obtained in the range of 30 °C to 100 °C, which probably indicates that the filler-matrix interaction at the interface plays a role at lower temperatures. As the temperature increases, the hindering effect of the interfacial interactions to polymer matrix expansion diminishes.

Table 5.3. CTE of the hybrid resins in different temperature ranges.

Sample	CTE ($\mu\text{m}/\text{m } ^\circ\text{C}$)	
	30 – 100 $^\circ\text{C}$	100 – 150 $^\circ\text{C}$
TGDDM/HHPA	64.9 ± 4.8	71.1 ± 1.8
5 wt.% OPS	64.4 ± 1.5	72.9 ± 1.7
5 wt.% OPS-Br	61.7 ± 1.9	69.9 ± 1.7
5 wt.% OBPS	63.1 ± 1.5	71.9 ± 1.6
5 wt.% OPS-13Br	65.0 ± 2.5	72.2 ± 2.9

5.2.4 Thermal stability

TGA curves depicting the percentage weight loss of the control, OPS and brominated OPS (5 wt.% OBPS) hybrid resins in nitrogen and air environments are shown in Fig. 5.8. Table 5.4 summarizes the thermal stability data of the POSS hybrids. The degradation profiles for the control and hybrid resins are similar. The degradation temperature, T_d is primarily influenced by the amount of inorganic content i.e. POSS cages within the resins. Thus, with low inorganic content, the hybrid resins show no significant improvement in the T_d . However, the overall char yield of the resin is improved due to the inclusion of inorganic POSS cages that degrade to SiO_2 but do not burn out. The improvement is more pronounced with OBPS. A slight drop in T_d in the 5 wt.% OBPS resin given in Table 5.4 is because that OPBS is less stable than OPS due to the weaker C-Br bond [123].

Fig. 5.8. TGA thermograms of the epoxy/POSS hybrids under (a) nitrogen; and (b) air atmosphere (– TGDDM/HHPA; ■ 5 wt.% OPS; ○ 5 wt.% OBPS; ▲ OPS; ◇ OBPS).

Table 5.4. Summary of thermal degradation data from the TGA curves.

Sample	Inorganic content (wt.%)	In N ₂ atmosphere		In air atmosphere		
		T_d (°C)	Char yield at 700 °C (%)	T_d (°C)	Mass at 550 °C (%)	Char yield at 700 °C (%)
TGDDM/HHPA	0.0	354	1.4	351	18.6	0.8
5 wt.% OPS	1.9	354	7.8	351	26.5	2.2
5 wt.% OBPS	1.2	350	11.8	349	29.7	2.4
OPS	40.3	518	79.3	481	79.7	36.3
OBPS	25.0	482	55.7	478	73.5	38.3

The oxidative environment clearly promotes the formation of a protection layer earlier, as shown by the shoulder between 400 °C and 600 °C, but the char yield at 700 °C is reduced. The hybrid resins show significantly reduced mass loss between 400 °C and 600 °C compared to the control resin, strongly suggesting that a protective barrier containing

POSS has been formed, which prevents the fast spreading of heat in the resins and hence decrease the decomposition and gasification rate. A slightly higher shoulder is observed for the 5 wt.% OBPS resin (29.7 % mass remaining), as compared to the 5 wt.% OPS resin (26.5 % mass remaining), at 550 °C. This indicates the action of bromine radicals bonding with radicals in combustion gases, thus reducing the fuel concentration and impacting the thermal degradation rate.

5.2.5 Surface properties

The synergistic improvements in thermal stabilities portrayed by POSS and the bromo groups may be explained by the change in the surface properties when brominated POSS are incorporated into the resins. These POSS nano-fillers consisting of organo-silicon and organo-bromine compounds are generally of low surface energy. When they are incorporated into epoxies, the resin surfaces can be enriched with the POSS nano-fillers with the effect of enhancing overall surface hydrophobicity. The surface properties of the nanocomposites were investigated by measuring the static contact angles at the surfaces and their calculated surface energies are given in Table 5.5. Compared with the control resin, the surface hydrophobicity of the nanocomposites are generally increased, with the contact angle up to ca. 94.2° when 5 wt.% OBPS was incorporated into the epoxy network. It is likely due to the bromo groups contributing to the further lowering of the surface energy of OPS which in turn made the surface of the resins more hydrophobic. It can be noticed that the polar component γ_s^p is more responsive than the non-polar component γ_s^d for the reduction of surface energy of the resins.

Table 5.5. Static contact angles (θ) and free surface energies (γ_s) of the epoxy hybrids.

Sample	$\theta_{\text{H}_2\text{O}}$ (deg)	$\theta_{\text{ethylene glycol}}$ (deg)	γ_s^d [*] (mN m ⁻¹)	γ_s^p [*] (mN m ⁻¹)	γ_s (mN m ⁻¹)
TGDDM/HHPA	80.2 ± 0.9	57.3 ± 1.0	19.2	9.6	28.8
5 wt.% OPS	80.2 ± 0.9	59.7 ± 0.8	16.4	11.0	27.4
5 wt.% OBPS	94.2 ± 0.8	73.8 ± 1.6	16.2	4.3	20.5

^{*} γ_s^d and γ_s^p are dispersive and polar components of the surface energy, respectively.

Qualitative XPS analysis with 5 wt.% OBPS resin provides further evidence of the brominated POSS enhancing the hydrophobicity of the resin surface. The XPS data in Table 5.6 shows that the free resin surface contains a higher percentage of silicon and bromine than in the bulk. The surface properties data demonstrate that by functionalizing the POSS with low surface energy organo-compounds such as bromine and phosphorous, the resultant POSS are able to migrate to the resin surfaces may assist in improving the thermal stabilities of the epoxy hybrids.

Table 5.6. Elemental compositions of 5 wt.% OBPS resin determined by XPS.

Region	Experimental composition (mol.%)				
	C	O	Si	N	Br
Free surface	69.6	17.7	9.2	1.8	1.8
Bulk	74.0	21.3	2.4	2.2	0.2

5.2.6 Summary

Novel POSS/epoxy hybrids have been prepared by incorporating brominated OPS nano-fillers into the epoxy resin. The dispersion of the nano-fillers in the epoxy resin is improved by attaching polar bromo groups onto OPS cages, evident from the SEM and WAXS data. However, TEM analysis reveals there is still some aggregation at the nano-scale level, possibly due to the POSS propensity for aggregation. Thermal and thermo-mechanical properties of the hybrids are not significantly affected by the nano-fillers. Fillers with larger specific surface area/aspect ratio behave slightly differently from those particles of spherical shape. However, TGA analyses show improved resin char yields with inclusion of POSS and increased mass loss retardation at high temperatures in an oxidative environment, demonstrating the synergistic effects brought about by the brominated POSS cages.

6 CONCLUSIONS & RECOMMENDATIONS

6.1 Conclusions

The aim of this thesis was to investigate the effect of incorporation of functional POSS compounds bearing multiple and single reactive groups, as well as non-reactive groups on resultant morphologies, thermal and thermo-mechanical properties of novel anhydride-cured epoxy hybrid resins, which to a large extent, has been achieved.

Anhydride-based POSS/epoxy systems with reactive POSS cross-linkers have been prepared. The findings obtained in cure kinetics analyses show a difference in the reactivity between OB, a POSS with multiple epoxy groups, and TGDDM, an epoxy containing catalytic amine sites towards HHPA, causing competing reactions with the anhydride, resulting in incomplete cure and inhomogeneity in the hybrid networks. DSC and morphological data indicate that the introduction of pre-mixing has positive but limited impact in mitigating the cure kinetics problem, as excessively long periods of mixing results in formation of POSS oligomers which are detrimental to the properties of the hybrid resins. The introduction of the two-stage thermal cure leads to moderate improvements in the cure and homogeneity of the hybrid networks and their resultant properties. Another mitigating method presented in Chapter 3 showed that kinetics difference can be effectively reduced by altering the POSS tether chemistry such that the two competing monomers become anhydrides, delivering promising improvements to the thermal and thermo-mechanical properties of the epoxy hybrids.

Mono-functional reactive POSS was introduced to reduce the kinetics difference between the different components experienced by the introduction of POSS cross-linkers

in the earlier part of the work. Novel anhydride-based epoxy hybrids incorporated with mono-functional POSS-imidazolium compounds (POSS-IMC) were prepared. Kinetic analyses and property studies revealed the synergistic traits of the POSS-IMC, which is able to act as an initiating agent to catalyze the epoxy-anhydride reaction at lower temperatures, and also to provide reinforcing effect to the resultant hybrid networks by acting as physical cross-linking points, hindering polymer chain motion during deformation.

POSS-IMC used as intercalating agents for montmorillonite clay in novel anhydride-based hybrids also yielded promising results. WAXS and morphological data show that large *d*-spacing of the modified clay galleries provided by the bi-layer stacking of POSS cubes allowed for improved diffusion and initiation of cure of the resin monomers in the clay stacks, promoting intercalation/exfoliation. Thermo-mechanical properties were enhanced with POSS forming pendent units in the network, providing nano-reinforcement effect and allowing for effective stress transfer between clay and the matrix, demonstrated by a ~20 % increase in the modulus with 2.3 wt.% POSS-imidazolium modified clay.

To eliminate the cure kinetics issue faced by reactive POSS, the incorporation of non-reactive POSS compounds into epoxy-anhydride system was investigated. Increased amount of compatible tethers per POSS led to improvements in the dispersion of the POSS fillers in the resin networks shown by WAXS and morphological data. The attachment of low surface energy groups such as bromine also provides positive synergism on the thermal stabilities of epoxy hybrids. Thermo-mechanical property data shows that the addition of POSS with poor interfacial interactions lowered the glassy moduli of the hybrids due to poor dispersion of the fillers as shown by the morphological studies. On the other hand, inclusion of POSS with improved interfacial interactions i.e. OPS-13Br did not alter the glassy modulus much. This suggests that non-reactive POSS

can be used to improve thermal stability of the resins without much detrimental effect of the thermo-mechanical properties provided that good nano-scale dispersion is achieved.

In conclusion, the significance of the work with reactive POSS compounds as cross-linkers lies in the fact that regardless of resin component types, it is necessary to minimize the kinetics difference between individual components before noteworthy improvements in properties can be achieved. Mitigating methods to reduce cure kinetics difference include a two-stage thermal cure and alteration of POSS tether chemistry. Apart from alleviating the kinetics problem, the approach of using mono-functional POSS possessing catalytic functions i.e. POSS-imidazolium also allows for the initiation of the epoxy-anhydride reaction at lower temperatures. This is noteworthy as it permits the cure to be tailored, eliminating or minimizing the need for external catalysts that will otherwise be required in traditional epoxy-anhydride systems, resulting in less complicated formulations. It has also been demonstrated as effective intercalating and reinforcing agents in epoxy/clay systems. The work with non-reactive POSS highlights the crucial importance of strong interfacial interactions between the matrix and the POSS fillers on improving the properties of the cured epoxy hybrids, which was brought about by the compatibility and dispersion of the POSS in the system. Incorporation of non-reactive POSS may also provide positive synergism to the properties of the resins such as thermal stability.

6.2 Recommendations for future research

POSS/epoxy nanocomposites continue to attract much research interest within the field of polymer nanocomposites. The effect of cure kinetics of POSS bearing aliphatic reactive groups such as epoxide on the properties of epoxy-anhydride systems has been

studied. It is recommended that future studies should focus on POSS bearing rigid reactive groups. The more rigid POSS structure may help to enhance the properties of the resultant hybrids, but the cure kinetics may be influenced by the steric hindrance brought about by the organic groups. Different epoxy-anhydride formulations may also be investigated.

Future studies on catalytic POSS surfactants in epoxy/clay hybrids are recommended to investigate the effects of POSS loading and compatibility on property improvements. Different types of POSS-imidazolium surfactants with cycloalkane groups may also be synthesized for improving the compatibility with ECHM. Catalytic POSS with rigid and flexible groups will also influence their packing structure in clay which ultimately has a bearing on the resultant resin morphologies. Their effects on thermal and thermo-mechanical properties of the epoxy hybrids may be examined.

The attachment of other types of functional groups on non-reactive POSS with view on compatibility improvement between individual components and increasing the strength of the interfacial interaction forces can be considered in future work. It is also worth to verify and quantify the effects of aspect ratio and specific surface area of functional POSS using different model systems.

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APPENDIX

A. List of publications resulting from this work

- 1) Teo, J. K. H., Toh, C. L., and Lu, X. (2011). Catalytic and Reinforcing Effects of Polyhedral Oligomeric Silsesquioxane (POSS)-Imidazolium Modified Clay in an Anhydride-Cured Epoxy. *Polymer*, Accepted.
 - 2) Teo, J. K. H., and Lu, X. (2009). Novel Anhydride-functionalized Polyhedral Oligomeric Silsesquioxane as Potential Nano-filler in Packaging Applications. In: *Proceedings of the 17th International Conference on Composite Materials (ICCM-17)*, Edinburgh, UK, 27-31 July 2009.
 - 3) Teo, J. K. H., Teo, K. C., Pan, B., Xiao, Y., and Lu, X. (2007). Epoxy/polyhedral oligomeric silsesquioxane (POSS) hybrid networks cured with an anhydride: Cure kinetics and thermal properties. *Polymer*, 48, 5671-5680.
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