INORGANIC ORGANIC COMPOSITE POLYMER COATINGS BASED ON FUNCTIONALISED POLYHEDRAL OLIGOMERIC SILSESQUIOXANES

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Inorganic Organic Composite Polymer Coatings Based on Functionalised Polyhedral Oligomeric Silsesquioxanes

A thesis submitted in application for the degree of Ph.D. by

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I, Duncan James Robertson, hereby certify that this thesis, which is approximately 32,000 words in length, has been written by me, that it is the record of work carried out by me and that it has not been submitted in any previous application for a higher degree.

I was admitted as a research student in October 2004 and as a candidate for the degree Ph.D in October 2005; the higher study for which this is a record was carried out in the University of St Andrews between 2004 and 2008.

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Abstract

A study has been undertaken with the aim of preparing appropriately functionalised polyhedral oligomeric silsesquioxane (POSS) compounds to be used in ambient-cure chemistry. Numerous epoxy-functionalised compounds have been designed and synthesised and these materials have been characterised in order to determine their chemical structure. These compounds have also been incorporated into existing polymerisation reactions to test whether these materials could be used in the protective coatings industry. A glycidyl-functionalised POSS compound was prepared and reacted with a series of amines to produce ambient-cured polymers which could be used in the coatings industry. There were also a series of experiments undertaken on these polymers to identify the processes at work and to test how they compare to industry standards. As a direct comparator to this work, another set of results was obtained with a cyclic-siloxane material incorporated into the systems in place of the POSS. A linear analogue was also tested. The reactions proved to be a success and an appropriate data-set was yielded.

During the synthesis of POSS precursors there are a series of residual materials produced. These materials have also been studied in this project. It was anticipated that these would behave in a similar way to the POSS compounds however the same functionality was never achieved as had been with the POSS. Ambient-cured polymers have also been targeted from a basic hydride-functionalised POSS compound and a

polybutadiene system. The appropriate reactions unfortunately never took place as anticipated but there were a series of tests undertaken to identify the processes at work.

A study has also been undertaken using near-I.R. to track the curing reactions. From this data, the extent of cure could be studied and the make-up of the reaction could be investigated in more detail.

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1. Introduction

1.1 Early siloxanes and silsesquioxanes

Siloxanes are a group of organic-inorganic hybrid materials using four different building blocks. The silicate $SiO_{4/2}$ group is the simplest and from this, up to three of the oxygen links can be substituted for an organic group R, leading to $RSiO_{3/2}$, $RSiO_{2/2}$ and $RSiO_{1/2}$ which can all potentially combine to give a range of different products.

Compounds which are synthesised from the $RSiO_{3/2}$ siloxane unit alone are known as silsesquioxanes [1]. Since it forms three siloxane linkages it can lead to a wide range of three dimensional structures, possibly the most notable being Polyhedral Oligomeric Silsesquioxanes (POSS).

1.2 Polyhedral Oligomeric Silsesquioxanes (POSS)

1.2.1 Background

Polyhedral Oligomeric Silsesquioxanes (POSS) are compounds which are multifunctional in nature and consist of a “cage-like” core of silicon atoms bridged by oxygen through hydrolytic condensation. These molecules have the general formula $[RSiO_{3/2}]_n$ where $n \geq 6$, always even and determines the size of the silicon-oxygen cluster. The name is derived from the term silsesquioxane which denotes that

the silicon atom is connected to three oxygen atoms and the prefix “oligo” which is used to indicate a small number of silsesquioxane links. Prefixes such as “octa” or “deca” indicate a specific number of links.

POSS were first prepared by Ladenburg in 1875 [2] during experiments involving condensation reactions, but were initially misidentified. A report by Meads and Kipping in 1915 [3] suggested that these reactions were of little use as they produced complex mixtures of materials. It was not until the 1950s and 1960s that further investigation was undertaken and progress made in the controlled preparation of POSS molecules [4, 5]. Since then, a large number of functionalised POSS have been studied and developed ranging from POSS bearing only vinyl [6] functionality to POSS-bearing metal species which are discussed in more detail later in this work.

POSS geometries are often described by the term T_n, where n represents the number of $RSiO_{3/2}$ groups present. The T originates from the three oxygen atoms bound to the silicon, in other words the silicon is tri-substituted and has a general formula of $RSiO_{3/2}$. This practice continues when the silicon is bonded to four oxygen atoms and the term Q_n is used where n represents the number of $RSiO_{4/2}$ groups present. The terms T_n and Q_n are used frequently in this field. It should also be noted that the terms D_n and M_n are used when the silicon is bound to two and one oxygen respectively.

The T_8 species is by far the most studied due to its (approximately) cubic shape and the fact that it can only be synthesised as one isomer. The first cubic T_8 POSS to be

reported was octamethylsilsesquioxane and was one of the structures isolated by Scott in 1946 [7]. Unfortunately he was unable to fully characterise it due to its low solubility in numerous solvents but its structure was confirmed in 1955 by Sprung [8] and Barry [9].

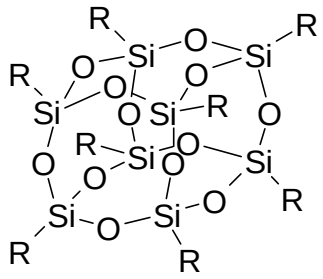

Figure 1.2.1 Cubic POSS species where R is one of a large range of organic groups

Many cubic POSS species have been prepared from the hydrolytic condensation of the appropriately functionalised silane [4]. Obviously all functionalised POSS with saturated alkyl constituents are inert to organic reactions but many POSS species with more useful, reactive groups have been prepared. For example, POSS molecules bearing vinyl or hydride functionality offer huge potential for further reactions which utilise the POSS core or allow further functionalisation with potentially useful groups. Manipulations of these groups are relatively simple which means a huge range of functionality is available.

The POSS core is extremely thermally stable, withstanding temperatures up to 400 ºC however it is susceptible to strong acids, bases and oxidising agents. This

obviously plays a large part in what modifications can be performed and manipulating the organic groups present without affecting the integrity of the inorganic cage can be difficult under certain conditions [9]. The fact that the POSS cage is so rigid and that it is highly electron withdrawing means that functionalisation is further complicated. This means that simple, high-yielding reactions need to be used to avoid the formation of partially and sometimes mixed functionalised species, which are extremely difficult to purify and manipulate further. Also, being able to achieve full functionalisation means that a yield approaching 100% is required, something which can be extremely difficult and another reason why simple manipulations are desired.

1.2.2 Metal Containing POSS

Transition metals can be incorporated into POSS to produce catalytically active species and these have become increasingly important in organometallic chemistry and heterogeneous catalysis [11]. Silica is the support most commonly used because its surface chemistry is relatively simple and well established compared to other supports such as alumina and metal oxides. Incorporating the metal can be achieved in a number of ways and are described below.

Incompletely-condensed silsesquioxanes (i.e. POSS species with one or more apices missing from the molecule) have shown great potential in catalysis, and a large number of “metallasilsesquioxanes” have been synthesised with both main-group and transition-metal complexes. Incompletely-condensed silsesquioxanes can be

produced during the process of producing discrete unit silsesquioxanes. As shown by Brown [12] and by Feher and co-workers [13] it is possible to prepare materials which are similar to these discrete unit silsesquioxanes but contain a number of silanol groups. The example shown in figure 1.2.2 shows three silanol groups which all surround the same missing silicon atom.

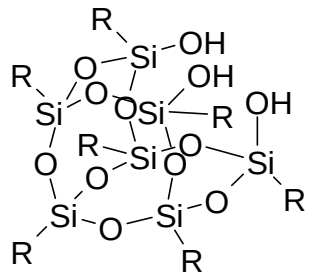

Figure 1.2.2 Example of three silanol groups surrounding a missing Si

It is also possible to leave two silanol groups by splitting an edge of a cube resulting in no loss of silicon as shown in figure 1.2.3.

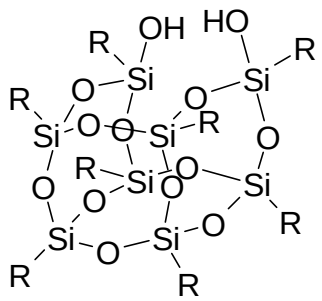

Figure 1.2.3 Example of two silanol groups being formed around the splitting of an edge of a POSS cube

There are two general methods for the preparation of such materials. One is to synthesise the compound from the silane in virtually the same way as completely condensed silsesquioxanes, but under conditions where complete condensation does not occur [14, 15]. This can lead to a variety of products but all contain the silanol groups where complete condensation has not taken place.

The other method of producing such compounds is from hydrolytic cleavage of a completely condensed silsesquioxane [16, 17]. This is achieved by the use of either a strong acid or base to partially destroy the cube in a controlled manner which is discussed in more detail later and can be seen in figure 1.2.7. This leads to the synthesis of materials that cannot be formed with the direct synthetic method.

These incompletely-condensed silsesquioxanes or partial cage silsesquioxanes are reacted in such a way that the open corner of the partial cube is capped (see figure 1.2.5). There has been extensive study in this area and there are examples of silsesquioxanes incorporating titanium [18], chromium [19], molybdenum [20], vanadium [21], osmium, [22] gallium, [23] thallium [24] and tungsten (see figure 1.2.4) [25] species leading to monomeric and dimeric molecules. It should be noted that some of these materials are essentially inert while others have been proved to be particularly useful, most notably in catalysis and as catalytic models. They are prepared from partial cubes hydrolytically condensed from silanes bearing cyclopentyl, cyclohexyl or cycloheptyl groups with a tri-functional metal species added to “cap” the open corner. Unfortunately no corner capped POSS have been prepared with functional groups that lend themselves to the preparation of extended

POSS networks. This means that preparing catalytically active porous solids is not possible in this way unless new corner capped species are prepared via the identification of suitable hydrolysable silanes or through somehow modifying the functionalities associated with existing corner capped POSS.

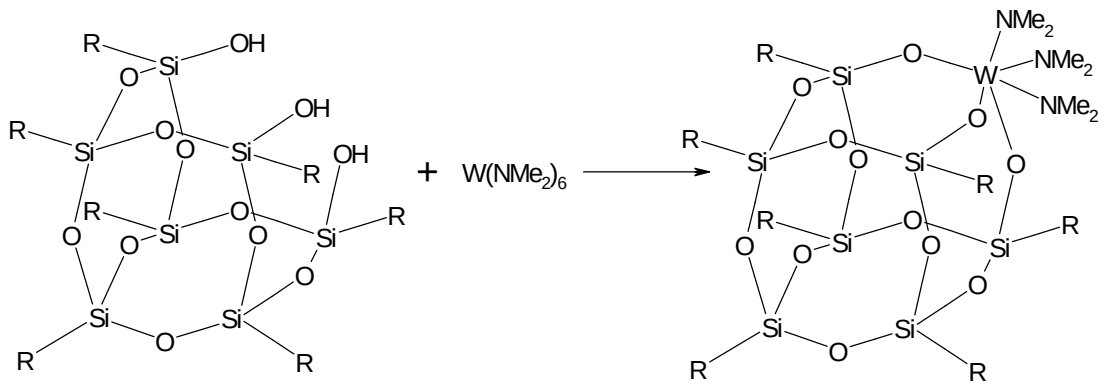

Figure 1.2.4 Corner capping a partially condensed POSS

Another route to incorporate metals into POSS cubes is to introduce the metal into the POSS structure during the formation of the cube itself. POSS cubes can be produced with alternating corners of silicon and a metal through hydrolytic condensation of a metal triol with a silicon triol [26]. Figure 1.2.5 shows such a species and here condensation occurs as for pure silanol precursors but the presence of a second species yields the mixed structure.

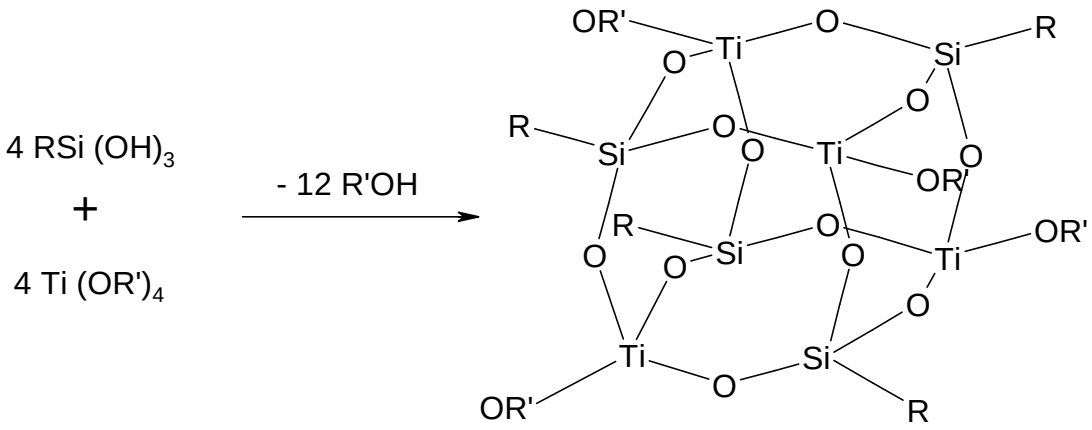

Figure 1.2.5 A mixed silicon – titanium POSS species

The applications of these species are greatly dependent on the functional groups attached to the metal and the silicon. Not only do they govern what can be achieved with the product but they also control how the POSS cluster forms. As with the corner capped POSS, the properties and thus the economic potential of these molecules vary wildly from the highly efficient, especially in catalysis, to the virtually inactive. Again, this depends on the metal incorporated and the related functional groups.

It has been shown that metals can be incorporated into POSS species by corner capping and during the actual process of the formation of the cube. Yet another way of including metals in the structure of POSS is by modification of a fully formed POSS molecule. Strong acids and bases can be used in such a way as to open the edges and/or corners of POSS cubes allowing the insertion of metals or heteroatoms [27, 28] (see figure 1.2.6). Obviously these molecules are being subjected to some extremely strong conditions and care must be taken to ensure the associated

functional groups are not susceptible to the cleavage process. Also, the reaction has to be controlled to ensure the POSS cube is not completely destroyed by the acid or base.

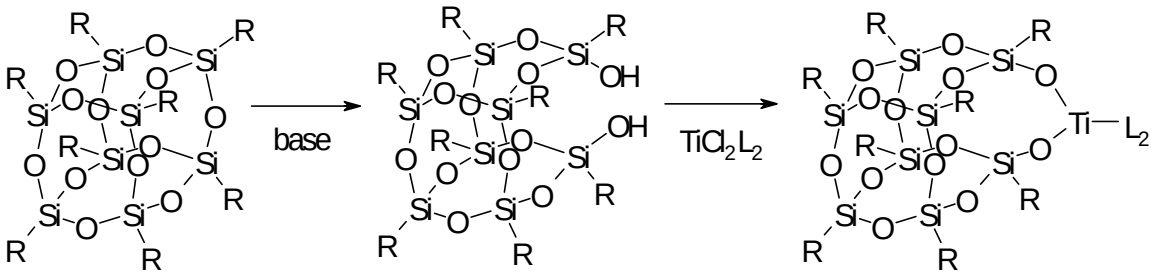

Figure 1.2.6 POSS cleavage followed by metal insertion

Again, the main use for these types of molecules would be in heterogeneous catalysis. Unfortunately, the cleavage technique has only been reported on cyclopentyl, cyclohexyl and cycloheptyl silsesquioxanes so intensive study is needed to see if this approach can be used with more useful functional groups present on the POSS cube [28]. This could lead to a whole range of new materials and would mean that catalytically active porous solids could be designed and synthesised.

1.2.3 Synthesis

POSS molecules can be prepared in a number of ways but all involve the hydrolytic condensation of a silane consisting of three hydrolysable groups and a fourth non-hydrolysable group. Trihalo- or trialkoxy- organosilanes are usually used which upon addition to water are hydrolysed to silanols which then go on to form the silicon-oxygen core of the POSS through condensation reactions. The non-hydrolysable

group remains intact and makes up the organic constituents on the corners of the POSS cage. The actual processes at work are very complicated and depend greatly on the functional groups present, the nature of the solvents and the reaction conditions [29].

The product formed can be “tailored” by the choice of silane used. For example, hydrolysis of trichlorosilane yields a mixture of T_8, T_{10} and T_{12} POSS while upon hydrolytic condensation of a silane such as 4-chloromethylphenyltrichlorosilane with water in acetone produces only the T_8 POSS. There are numerous other ways that conditions and reactants can be controlled to yield many other types of silsesquioxanes but this project will deal mainly with the T_8 POSS.

As is discussed in the project aims and objectives (section 1.6) the silsesquioxanes dealt with in this work are to be incorporated into ambient-cure protective coatings. Any coatings yielded would possibly be used in an under water capacity on things such as ship hulls and oil pipelines to see if the POSS cube increases any of the properties associated with well established protective coatings. In order to obtain POSS compounds which can take part in curing reactions then the appropriate functionality must be available. POSS functionalised with different organic groups have been well documented and many examples have been reported. These can be made directly during the hydrolytic condensation reactions or by synthetic manipulation of pre-formed POSS.

As previously stated, POSS compounds are made from a silane with three hydrolysable groups and a fourth non-hydrolysable group. This means that if the desired functionality is to be achieved during the synthesis of the POSS cage then it must not be so reactive that it reacts with the three, already reactive hydrolysable groups, but it must be reactive enough for further manipulation to be possible once the POSS condensation has taken place. The main organic groups that are produced in this way are hydride [30] (see figure 1.2.7) and vinyl functionality [6]. These compounds are extremely important to the field and are often used in the synthesis of POSS polymers and co-polymers due to their relative reactivities but are more often used as a precursor to other, more specialised functionalities. One draw-back is that these reactions are generally very low yielding which may have something to do with the desired functionality being able to withstand the hydrolytic condensation process.

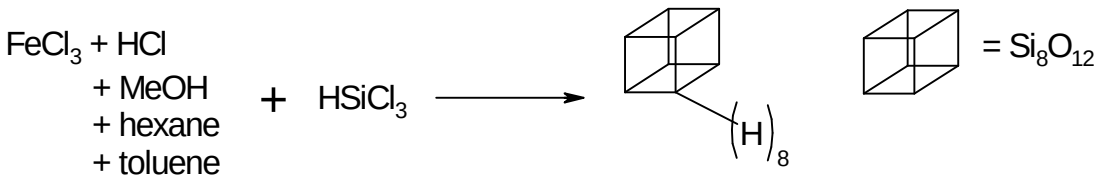

Figure 1.2.7 Example of the synthesis of hydride-POSS [30]. Note the illustration of the final POSS indicates that a hydrogen atom is connected to all eight corners of the POSS ‘cube’.

There are a huge number of chemical manipulations that can be carried out on POSS compounds. An extremely powerful and useful reaction is hydrosilylation. This is the reaction of a silicon hydride group with a carbon-carbon double bond which then

results in the formation of a silicon carbon bond (figure 1.2.8). There are many advantages to this reaction. They are generally carried out under very mild conditions, are very high yielding and are very repeatable. They use platinum, palladium or rhodium containing catalysts with the most successful being the platinum-containing Karstedt's and Speirs catalysts.

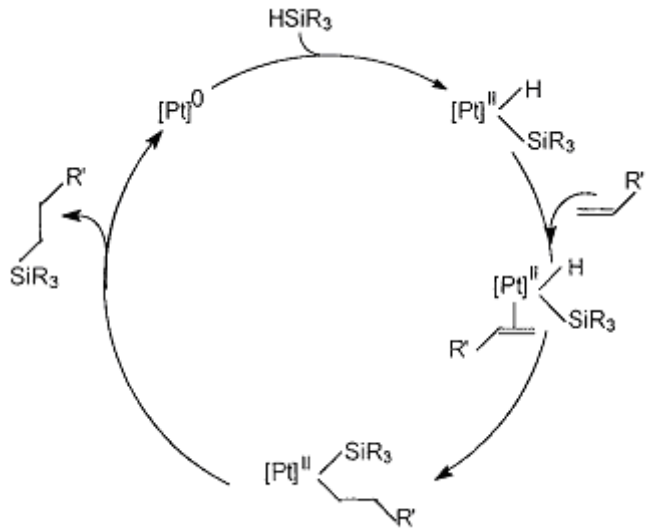

Figure 1.2.8 Pt catalysed Chalk-Harrod hydrosilylation mechanism [31]

Another advantage of this reaction is that both hydride and vinyl functionalised POSS can be utilised which are two of the most commonly used POSS starting materials owing to being relatively simple to prepare. Hydride POSS is most commonly used but another route to a target molecule can be via a silane with a silicon hydride group and vinyl-POSS. This means that the preparation of suitably functionalised POSS molecules can be prepared via either route which lend themselves to further functionalisation.

POSS can be subjected to a large number of organic manipulations and another particularly useful one is cross metathesis [32]. This involves exchange of functionality between vinyl containing POSS and molecules with carbon-carbon double bonds.

There are many more chemical manipulations which can be undertaken on POSS such as simple epoxidations [33, 34], Diels-Alder reactions [35] and of considerable use is the anti-Markovnikov addition of hydrobromic acid to create a linear alkyl halide functionalised POSS [36]. This can be converted to a Grignard reagent and used in numerous other reactions or can be used directly themselves in suitable substitution reactions.

As mentioned previously, POSS clusters are susceptible to strong acidic and strong basic conditions. Obviously this limits the number of possible chemical reactions to a certain extent and can restrict the range of synthetic options available. When planning a chemical manipulation of a POSS system this has to be taken into account so there are some restrictions to what POSS molecules can be subjected to.

1.3 POSS Polymers and Copolymers

Due to their versatility, many different types of POSS molecules can and have been prepared. They contain one or more covalently bound functional group which is suitable for polymerisation, surface bonding, grafting or other transformations. A

massive advantage that POSS has over other organic compounds is that they release no volatile organic components, making them environmentally friendly.

Over the last decade more and more research groups have begun working with silsesquioxanes, in particular POSS, and this has lead to POSS being synthesised on a much larger scale and becoming commercially available [37]. This has meant that a selection of POSS chemicals now exist which contain various selections of reactive and / or non-reactive substituents. With this amount of functionality available POSS can be easily incorporated into common, well-known plastics and polymers via copolymerisation, blending or grafting [38]. The incorporation of POSS into polymeric systems can lead to dramatic improvements in properties which include increases in use temperature [39], scratch resistance [40] and oxidation resistance [41] as well as reductions in flammability and heat evolution [38, 42]. It should be noted that the incorporation of POSS does not lead to dramatic changes in the reaction conditions or processing of these polymeric systems, these molecules can be simply “dropped-in” to the system in question – monomers are commonly mixed and copolymerised. As long as the POSS monomer is soluble in the monomer mixture, it will be incorporated in a true molecular dispersion in the polymer. Phase separation can be a problem but if the correct conditions are used this can be overcome.

Due to their similarity to frameworks found in some zeolites, they can be used as building blocks in the synthesis of porous polymers. Their multi-functionality can be used to synthesise homopolymers and copolymers. They can form networks by linking at the corners of the POSS cube as shown in figure 1.3.1. These result in

porous polymers and since the functionality on the corners can be tailored relatively easily it can be seen that different pore sizes can be formed. For example, large functional groups would lead to the POSS cubes being further apart, leading to larger pore sizes.

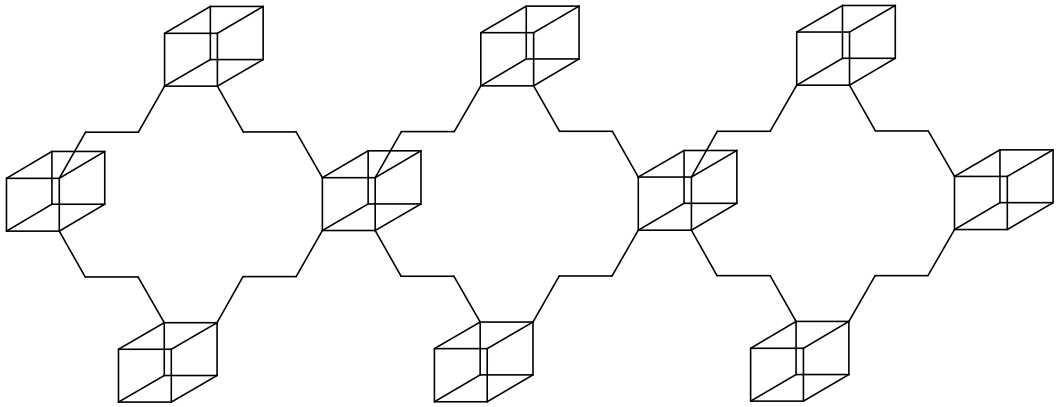

Figure 1.3.1 A simplified schematic of a POSS network copolymer. Only one "layer" is shown here for clarity

POSS molecules also have the opportunity to take place in the design and synthesis of micro- and mesoporous materials. The most facile and common approach to this is via the hydrosilylation reaction between a vinyl group on one POSS molecule and a hydride group on another. This means that POSS networks could be developed to make a certain type of porous system and could be tailored to a certain extent which is very desirable to a number of applications.

Copolymerisation reactions have been studied between POSS and non-POSS molecules in the hope of yielding a variety of useful materials. This is what the main

body of this work will look at and discuss, namely the polymerisation of octa-epoxy functionalised POSS with amine-containing molecules [43]. Epoxy polymers are well known and are widely studied due to their excellent thermal and mechanical properties. Incorporating the POSS cage offers the possibility of further improving these properties as well as improving the physical and chemical properties. This will be discussed in detail in another section of this work.

As discussed, POSS have found applications due to their multifunctional nature, making them ideal cross-linking agents, but they can also be used as hard or stable blocks to modify or improve the properties of well-known polymeric materials. Due to their versatility, they can be incorporated into a number of different, “conventional” polymeric systems and can introduce new properties such as improved physical strength. The temperature stability of certain polymers has been shown to increase, which has meant that these systems can be used as thermal retardants in heat protective coatings for surfaces and clothing [44, 45].

1.4 Coatings

1.4.1 Background

Coatings and paints have several purposes such as the prevention of corrosion by either including an anticorrosive pigment or simply by providing an adhesive and impermeable barrier, providing either stick or non-stick properties, impact and

scratch resistance, resistance to contamination, the list goes on. No matter what the desired properties are, they can be generally expressed and calculated in terms of:

(i) energy savings

(ii) reduced downtime

(iii) increased lifetime

(iv) capital savings

(v) materials substitution [46]

Examples of the importance of producing and developing new coatings can be seen in the marine industry. A new tanker which is uncoated would suffer severe corrosion in five years or less, however an adequately coated one might avoid serious repair for 15 - 25 years [46]. This shows that by coating the tanker the lifetime is at least tripled, saving on the materials, time and energy to build another tanker.

It should be noted at this point that coatings manufacturers, ship owners and operators are not the only people involved but there are also environmental issues to be aware of. There are a number of chemicals and particular molecular species which have skirted with controversy in terms of their effects on the environment when used in protective coatings, particularly on ships and other marine applications. Tributyl tin is an example of a chemical which was extensively used in the marine industry as an antifouling agent but which was having large negative effects on the environment [47].

Coatings also play an important role in protecting structural metals from corrosion. Iron and aluminium are the most abundant metals in the Earth's crust, comprising about 5.8 % and 8.8 % respectively [46]. The major component of the cost of producing these is the energy required to reduce the naturally occurring ores to the metallic state. They are also thermodynamically unstable in our atmosphere and tend to revert to their original oxides as corrosion products. Obviously these materials need to be protected to make them commercially viable.

Not only do coatings play a large part in protecting metals that are readily available but this also means that more precious metals which are rare and expensive do not need to be used as often. Coated steel has "added value" in that it can perform many of the functions which would require the use of much more expensive metals and alloys such as copper, bronze or stainless steel or more expensive coating processes such as electroplating with expensive metals such as nickel or chromium, plasma or ceramic coating [46].

As can be seen, coatings and barrier materials are extremely important today, not only in terms of economics but the environment also.

Good coating and barrier properties extend from polymers with strong intra-chain forces that induce high packing which in turn hinder gas diffusion. Properties such as strong hydrogen bonding, chain alignment by extrusion and high degrees of crystallinity all provide routes to high performance coatings. Another approach is to add an easily dispersed second phase, which can be organic or inorganic, to the

system such as clay particles or simply silica. This is quite a simplistic approach which basically adds to the durability of the coating.

Another method of producing barrier materials is to produce bilayer films where transport across the interface is difficult, thus leading to high performance barrier materials [48] with increases in mechanical strength and improvements in impact properties [49]. These bilayer systems can include the introduction of an inorganic phase which can include metals such as aluminium in what are called metallized layers.

Another novel approach to produce composite films and coatings utilises a “self-assembly” technique [50]. Ultra-thin films and coatings can be produced in this way and a number of novel and unique materials can be designed and synthesised. The layer-by-layer self-assembly technique is a good approach as it allows the sequential assembly of multiple layers of oppositely charged materials on a range of supports and substrates. Films produced in this way have been designed with unique magnetic [51], catalytic [52] and optical properties [53]. Reactive surfaces can also be produced in this way as well as the ability to control porosity and permeability.

Clearly the design, synthesis and application of a secondary phase adds to the difficulty and expense of processing and obviously these benefits need to be economically viable in order for them to be used.

1.4.2 POSS in Coatings

There are two main routes by which silsesquioxanes can be incorporated into coatings. One is to attach the POSS cube onto an organic chain polymer in such a way that it is essentially “hanging off” the polymer backbone in the hope that the essential properties of the coating are improved. In fact, POSS incorporated into barrier materials and coatings is based overwhelmingly on this method and is known as “pendant POSS” (see figure 1.4.1) [54]. This approach leads to the study of the effects of a well-defined, symmetrical inorganic additive connected to a variety of organic polymer backbones. Due to the reactivity of the POSS being so well defined, it can be controlled to a certain extent, which means that dispersion of the POSS cubes in the polymer can be controlled. This leads to polymers which are simple to process due to a lesser degree of cross-linking, but that also lead to some striking improvement in properties. When used in this way POSS can increase thermal stability in terms of glass transition temperatures and decomposition temperatures [55] and many other properties such as increasing abrasion resistance [56] and increasing gas permeability [57].

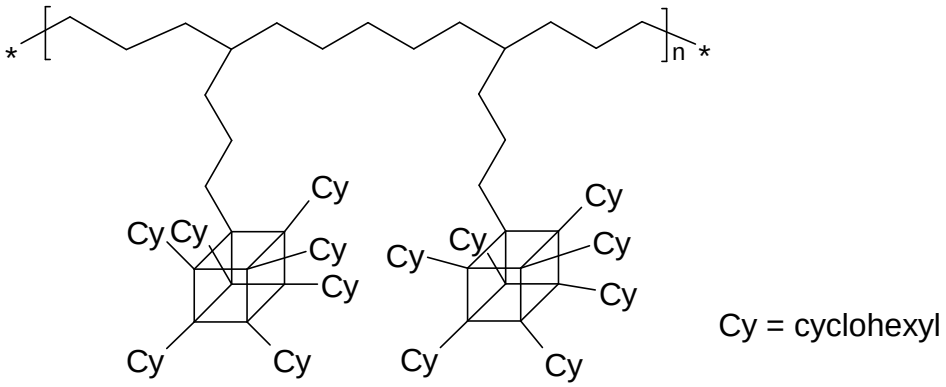

Figure 1.4.1 An example of POSS tethered to a polymer backbone or pendant POSS

Incorporating a nanometer sized building block in this way brings about a local chain reinforcement. It has been suggested by Lichtenhan *et al.* [58] that POSS-POSS interactions play a dominant role in the physical properties of the resultant polymers. These properties are enhanced due to formation of a physical network of the POSS and it affects the polymer chain mobility through POSS aggregation which then leads to changes in their thermomechanical properties [59]. Relatively small amounts of POSS (ca. 10 wt%) were observed to strongly raise the glass transition temperatures of the polymers.

One of the most well defined and studied systems is the POSS-norbornyl system of Mather and Haddad [60] which continues to be used to study POSS interactions at the molecular level (see figure 1.4.2). They showed that slight increases in the weight percent of POSS in the system can lead to dramatic increases in the glass transition temperatures [55].

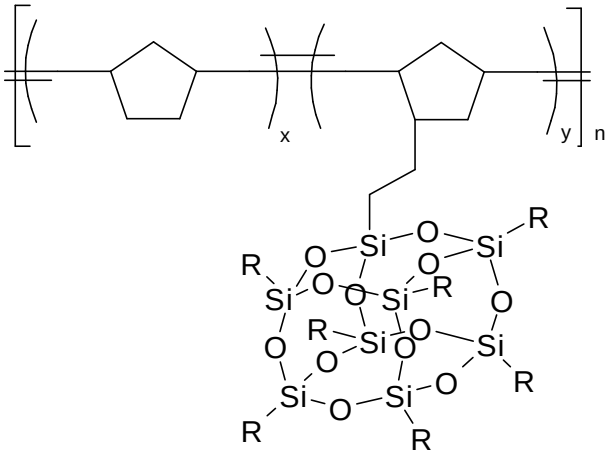

Figure 1.4.2 Repeat unit from the POSS-norbornyl system [60]

POSS attachment has been undertaken in this way on numerous other polymer backbones such as polysiloxane [58], polymethacrylate [61], polyolefins [62] and polystyrene [63] leading to increased glass transition temperatures, increased decomposition temperatures and modulus, reduced flammability and increased gas permeability [57]. This shows that POSS incorporated in this way is an extremely powerful technique and one which is relatively simple to undertake.

The other method of incorporating POSS into coatings and other barrier materials exploits the number of possible functional groups available. Octa-functionalised POSS species can be used to form three dimensional structures with the silicon cores linked by a series of organic bridging groups. The exact structure of such polymers is not fixed and despite the possibility of forming links to eight other similar molecules, steric and kinetic factors often make this unlikely or even impossible.

There is relatively little published in the literature regarding cross-linking POSS molecules in such a way that they are a fundamental part of the polymer network in coatings. The work undertaken in this PhD project is to incorporate octa-funtionalised POSS molecules into already existing ambient cure reactions to observe what these systems add to coatings, if anything.

The two different routes to obtaining coatings mean there are two different types of POSS molecules to be produced, isolated and characterised. Obviously POSS with seven inert and one reactive site is desirable in the pendant processes and these can be produced on a large scale or purchased in relatively large amounts (see figure 1.4.3) [37]. This is in stark contrast to the octa-functionalised POSS species which can be difficult to synthesise and isolate on a large scale and can be expensive to obtain from commercial sources [37]. This is a huge advantage for the pendant systems and is one of the main reasons that there has been so much study into this area.

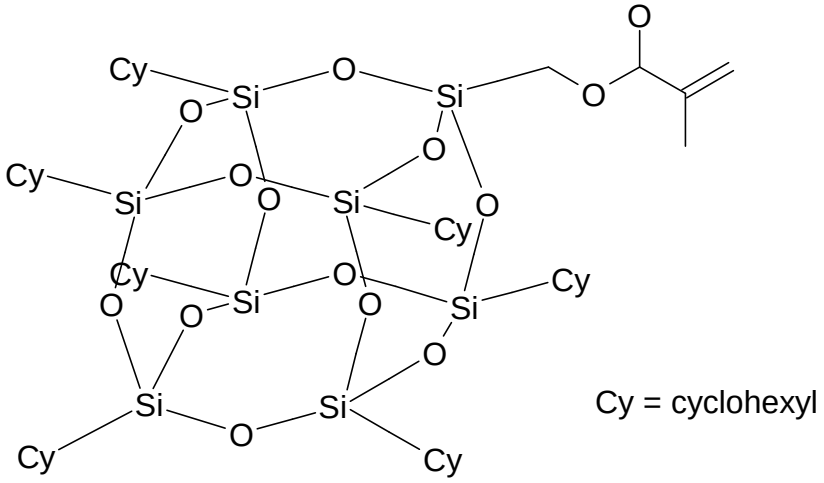

Figure 1.4.3 An example of a “monofunctional” POSS compound with one reactive site

1.4.3 Epoxy-cured Coatings

Coatings and barrier materials based on epoxy resins are used a great deal in coatings and other structural applications. There are a great number of applications available due to their excellent adhesion qualities to a variety of different substrates [64], good chemical and corrosion resistance, as already discussed, excellent electrical insulation [65] and thermal stability.

The main reason epoxy resins have become so popular in the coatings industry is due to how important high chemical and corrosion resistance is as well as adhesion qualities. This has meant that epoxy-based materials and resins have become one of the key components in the coatings industry. Although not covered in this piece of work, recent growth in the electronics market has increased the demand for epoxy

resins in the manufacture of printed circuit boards and compounds for semiconductor encapsulation [66].

Commonly in the coatings industry, epoxy resins are synthesised first as oligomers with epoxide end groups which are capable of undergoing further polymerisation to form complex network polymers. There are many examples of different oligomers which are formed by the step-reaction polymerisation of a diphenol and an epoxide containing compound [67]. This then leads to the formation of glycidyl functionality, something which is dealt with in a lot more detail in this project.

Further polymerisation of these compounds can then take place to form cross-linked polymers. Carboxylic acid anhydrides are commonly used for this but in the majority of cases, amines are used. The amines react via a simple nucleophilic addition to the epoxide ring [68].

This particular avenue of work has been the main focus of this project. Epoxy and glycidyl functionality have been targeted with a view to producing novel coatings materials. There is not a lot in the literature with regards epoxy-POSS systems being used in the coatings industry so being able to use these sometimes very difficult to manipulate compounds in such a way may be very challenging.

1.5 Other Applications

There are a huge number of applications, realised and proposed, available to POSS due to its shape and functionality. The number of applications is also steadily increasing as more and more research groups study POSS. They also lend themselves to a huge variety of applications based on their versatility, their physical properties and their multiple functional groups.

One application for POSS molecules is in the production of dendrimers. Dendrimers are globular molecules with functional branches radiating from a central core and are commonly used as catalyst supports and have a large number of active sites [69]. Due to their large size, they can be easily separated from a substrate by simple filtration making them extremely useful molecules [70]. Typically, dendrimers have up to six reactive sites to which branched organic 'arms' are attached to form a first generation dendrimer. Subsequent arms can then be attached to form second generation dendrimers and so on. When the dendrimer is of the appropriate size the arms are terminated with appropriate functional groups which are extremely important as the steric interactions between them are vital to the dendrimer's properties. POSS can be used as the central core of a dendrimer molecule [71, 72]. Obviously it has eight active sites and a very high level of organic arms can be achieved through relatively few chemical manipulations. Also, the dendrimer can be built out in three dimensions yielding a globular structure which, by the second generation, has 72 end groups. This is in direct contrast to a second generation dendrimer based on a tetrahedral core which can only have a maximum of 36 end

groups. This means that a large number of catalytic materials can be supported on the POSS-based dendrimer which can lead to interesting effects on catalytic selectivity and activity [73].

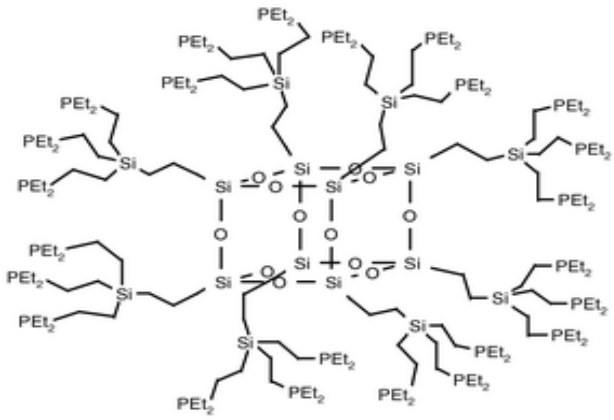

Figure 1.5.1 Phosphine terminated dendrimer molecule [72]

POSS cubes can lend themselves to be used as molecular building blocks in the preparation of extended networks. They are ideally suited for this as they are extremely thermally stable and robust, their functional groups mean linking them together is simple and their cubic nature is perfectly suited to the preparation of porous solids and molecular sieves. A number of different approaches can be undertaken to yield different types of solid such as functional group selection and the desired networking mechanism. For example, a reversible linking mechanism such as metal co-ordination or hydrogen bonding means that the structure formed is not fixed and can be directed towards whatever order is desired. Existing molecular sieves are obtained through kinetically driven synthesis whereas the main guiding influence for

these materials is thermodynamic stability. This means that POSS extended networks can be tailored to suit a range of applications and within each application there is a large amount of flexibility.

POSS compounds can be used as models for the silica surfaces of larger compounds [74]. As discussed earlier, other species can be incorporated into POSS structures and the bonding around these should be similar to other silica surfaces. This means that information can be obtained about systems which could not previously be studied due to poor thermal stability.

These materials can also be used as a filler compound within certain products as a replacement for silica [37]. The fixed structure of the inorganic cluster possesses a lower density than that of silica and at the same time has similar chemical properties. Also, the silsesquioxanes can be disposed of as easily as silica. All of this has led them to be used more extensively in lightweight commercial materials.

Silsesquioxanes bear a strong resemblance to the basic building blocks found within zeolites [75] (figure 1.5.2) in terms of both structure and chemical composition. Therefore it is a possibility that polymers and copolymers synthesised from silsesquioxanes could find similar applications [76].

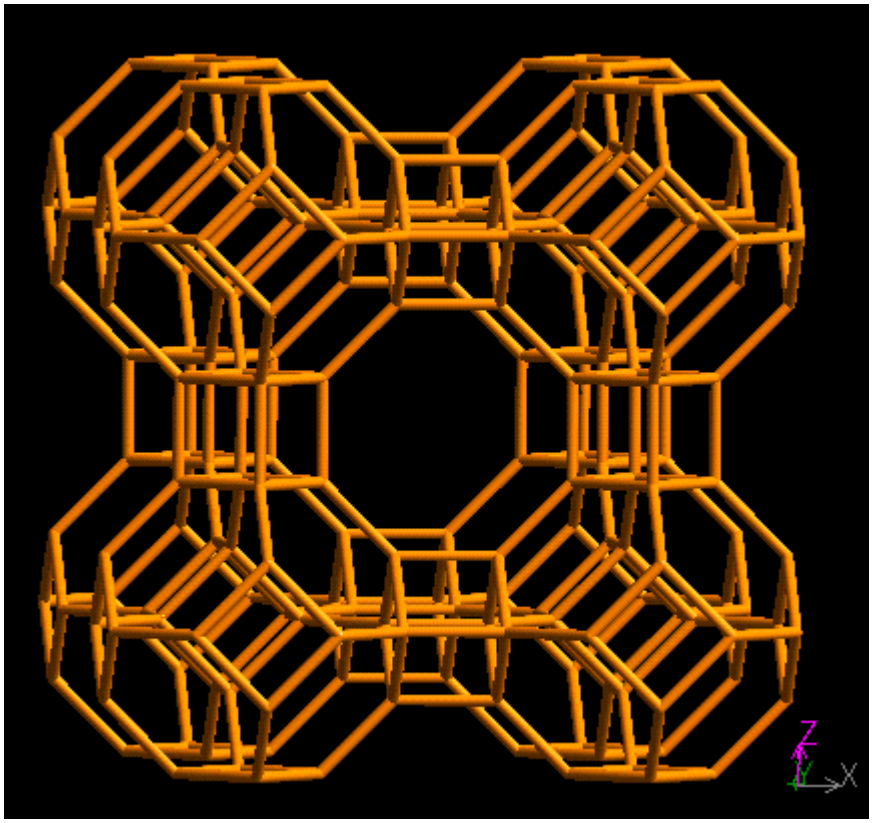

Figure 1.5.2 An example of a zeolite framework, zeolite A (LTA) [75]

There is one fundamental difference between the two and that is the fact that zeolites require a cation to counterbalance the negative charge on the aluminosilicate framework. This can be advantageous to many catalytic processes but there are other situations where such conditions are not suitable. In these cases a silsesquioxane-based copolymer could be used which has no charge.

Another difference between the two is in their preparation. The time required for the synthesis of a zeolite can be extensive and sometimes requires the presence of conditions which may be difficult to achieve to prepare the intended structure [76]. Silsesquioxanes could offer more simplicity but as already discussed, synthesis is not

always straightforward. Also, silsesquioxane copolymers do not possess the well defined structures of zeolites. A well defined structure is not always vital to a system but selectivity might be reduced if a zeolite is not used which can be crucial depending on the requirements of the solid.

There are also a huge number of applications for POSS in the design and synthesis of polymeric materials. They make ideal cross-linking agents due to their multifunctional nature and the range of functionalities available. They can also be used in polymeric systems as a different form of silica “filler” or as a strong, stable material to enhance the properties that the polymer already possesses. It was the intent of this work to see exactly what POSS can add to coatings, especially coatings which are used in the marine industry.

POSS compounds and systems are being used in a range of new and novel techniques and the range of these new applications is quite staggering. POSS-based nanocomposites have good biocompatibility and anticoagulation and so can be used for biomaterials [77]. For example, Kannan *et al* [78, 79] recently developed a nanocomposite of POSS/poly(carbonate-urea)urethane for use in cardiovascular bypass grafts and the microvascular components of artificial capillary beds.

Other biological applications for POSS compounds include uses as the probe in resonance light scattering (RLS) measurements in the detection of DNA [80] and in the production of organic light-emitting diodes (OLEDs) [81].

POSS species are also finding applications in the electrochemical field as Xiong *et al.* [82] have shown that POSS/aniline polymers have increased electrochromic contrast compared to polymers with no POSS incorporation. Electrochemical stability was increased also. A similar study was undertaken by Imae *et al.* [83] with a carbazole substituted POSS which showed that these types of materials could be used for novel types of photo- and electroactive materials.

POSS compounds have also recently found applications in space technology as it has been shown that certain POSS polymers and copolymers are space survivable [84, 85]. Recently, there has been study into using sulfonated POSS as hybrid membranes in direct methanol fuel cell applications [86] and the use of POSS in high performance holographic gratings which are used in holographic recording [87].

1.6 Project Aims and Objectives

The main aim of this project was to design and prepare POSS molecules which would take part in ambient-cure chemistry. It was hoped that such molecules would be able to be incorporated into protective coatings in order to see what POSS can contribute to this field.

The primary objective was to prepare the actual POSS molecules which would be used over the course of the project. If suitable molecules could be produced it would then be possible to test them for their suitability to take part in polymerisation reactions under ambient conditions.

As described earlier, there has been considerable work using ‘pendant POSS’ species in polymers and these have shown some very striking and potentially important improvements in materials property. However, there has been much less work on the incorporation of POSS molecules through more than one connection to the polymer backbone. A major goal of this project was therefore to prepare POSS molecules with eight functional groups suitable for incorporation into ambient cure polymers. This requires significant work on the synthesis of these compounds and their subsequent functionalisation as well as their polymerisation reactions to be completed.

The second objective was to test any polymers produced in the same way as industrially produced coatings. This would show how the performance of any

products achieved with POSS incorporated, compare with more established paints and coatings.

A secondary aim of the project was to investigate the polymerisation reactions at work using a number of different approaches including varying the stoichiometry of the polymerisation reactions and the use of near-I.R.

As with many projects of this type it is very difficult to foresee where the work will lead so there were also a number of different reactions and ideas which were investigated. The strategy undertaken as part of this project was therefore to survey the particular types of POSS species that are available, choosing the ones most likely to be useful in an industrial setting before completing the further work.

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2. Experimental Techniques

2.1 Air and Moisture Sensitive Synthetic Chemistry

For air and moisture sensitive chemistry standard Schlenk techniques were used. All reaction vessels and syringes were oven dried before use and all solvents and liquid reactants were either obtained dry or were dried using established procedures [1].

For all air and moisture sensitive reactions a Schlenk line was used which was fitted with a Drierite (anhydrous calcium sulphate) column which argon passed through on entering the line. All Schlenk glassware which was used was oven dried before use, sealed with a rubber seal and evacuated of air and refilled with argon three times. Once the inert atmosphere had been obtained solvents were added via a syringe which had been stored under a dry, inert atmosphere. Each time a syringe was used it was filled with argon and evacuated three times as with the reaction vessel. All solid reagents were added to the reaction flask under a steady stream of argon.

When a reflux was set up a condenser, which had been oven dried before use, was fitted under a steady stream of argon. Argon was passed over the reaction and through an oil bubbler to ensure an inert atmosphere was maintained throughout.

2.2 Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) spectroscopy is a valuable tool in analysing materials for the organic and inorganic chemist. Structural information is yielded from the analysis of nuclei with non-zero magnetic moments [2].

Atomic nuclei with an intrinsic angular momentum have a nuclear spin (I) and the presence of a spin makes these nuclei behave like bar magnets. When a magnetic field (B_0) is applied these nuclei adopt 2I + 1 orientations. Those nuclei with odd mass numbers have nuclei spins of 1/2, 3/2, 5/2 etc. In the solution state ^{1}H and ^{13}C are by far the most important nuclei and both have a spin of 1/2. This means that these nuclei only have two orientations, a low energy orientation when aligned with the field and a high energy orientation opposed to the magnetic field. This difference in energy is given by equation 2.1:

$$\Delta E = h\gamma B_0 / 2\pi$$

Equation 2.1 The energy difference between low and high energy orientations

Where γ is the magnetogyric ratio (a constant which differs for each nucleus, which essentially measures the strength of the nuclear magnets) and B_0 is the strength of the magnetic field [2].

When the energy difference between these orientations is matched by a radio frequency signal which is applied to the system, some of the low energy nuclei are

promoted to the high energy level. This frequency, called the resonance frequency is given by:

$$\nu = \gamma B_0 / 2\pi$$

Equation 2.2 The resonance frequency in Hertz

The energy that is emitted as the nuclei relax to the ground state is measured minus a small portion which is absorbed.

The method used to obtain NMR spectra is Fourier Transform NMR (FT NMR) spectroscopy. The FT NMR spectrum is measured by applying the radio frequency signal as a single pulse that generates an oscillating magnetic field (B_1) at a right angle to the applied magnetic field (B_0). Initially, the sample being analysed has a net magnetisation in the direction of the applied field which is disturbed by the application of the pulse and its oscillation is detected. This oscillation has a distinct frequency which is the difference between the NMR resonance frequency and the excitation frequency. As the magnetisation oscillates it decays as relaxation allows it to return to its ground state. This signal is known as the free induction decay (FID) which after Fourier transformation (FT) yields the nuclei's frequency or chemical shift spectrum.

The frequency at which a nucleus comes into resonance depends on two things, the strength of the applied magnetic field and the magnetic environment experienced by the nucleus. Each nucleus has a very different local magnetic field which is affected by the electrons which surround it. This means that each chemically distinct nucleus

comes into resonance at a slightly different frequency. In order for these signals to have any true meaning they have to be compared to a standard. The common standard for ^{1}H, ^{13}C and ^{29}Si NMR is tetramethylsilane as it only has one signal (which appears at one extreme of the spectrum), is inert, volatile, non-toxic and cheap. The signals obtained are described as having a chemical shift (δ) from the standard frequency and are measured in parts per million (ppm).

NMR can separate and map chemically distinct nuclei but in ^{1}H NMR spectra the absorption of the signal is proportional to the number of protons coming into resonance at that frequency. This means that the area under the absorption peaks are proportional to the number of protons being detected in a particular environment. Unfortunately the same phenomenon does not occur in ^{13}C spectra because the different nuclei cannot relax to equilibrium between successive pulses. The peaks that are produced are not always simple, singular peaks. It is very often the case that peaks produced split into multiple peaks due to coupling between neighbouring or nearby magnetic nuclei. The magnetic field produced by one nucleus affects the magnetic field of neighbouring nuclei and in the case of first order ^{1}H-^{1}H coupling, if a carbon is connected to another carbon with n identical hydrogens its signal splits into n + 1 peaks. For example a proton which is bonded to a carbon in an aliphatic chain which is connected to a methyl group with identical hydrogens will yield a signal which will split into a quartet. The ratio of the intensities of the peaks are given by the coefficients of the terms in the expansion of $(x + 1)^{n}$, therefore in the above example the ratio would be 1:3:3:1. Protons that are further than two carbon

atoms apart don't usually couple, only sometimes if they are separated by a π bond, which means that connectivity between the atoms in the molecule can be established.

All solution NMR spectra were recorded on a Bruker Advance 300 spectrometer operating at the appropriate frequency.

2.3 Thermal Studies

A number of different thermal techniques were used over the course of this work which yield information on a number of different thermal properties including melting points, glass transition temperatures, flammability and thermal stability. The main techniques used here are Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA) and Thermogravimetric Analysis (TGA). Each technique is described in more detail below.

2.3.1 Differential Scanning Calorimetry (DSC)

DSC is a technique which is used for the quantitative study of thermal transitions in polymers.

A sample and an inert reference are heated, sometimes in an inert atmosphere, and thermal transitions in the sample are detected and measured. The sample holder is a small aluminium pan and the reference consists of an empty pan. Sample sizes can vary from 0.5 – 15 mg and the pans are commonly heated at a rate of 10 ºC/min. The

sample and the reference each have their own heater and energy is supplied to each to keep the temperature of the sample and the reference constant. The electrical power difference between the sample and the reference ($d\Delta Q/dt$) is recorded and is plotted against temperature.

The plots obtained are called thermograms and yield information such as glass transition temperatures, which appear as inflections or a shift in the initial baseline due to the increased heat capacity, and melting points which appear as peaks which are directly related to enthalpy changes in the sample [3]. This means that measurements such as extent of reaction, heat capacities and enthalpies of reactions can be investigated.

2.3.2 Thermogravimetric Analysis (TGA)

TGA is a technique which measures the loss of mass in polymers and porous materials. It involves weighing a sample whilst it is heated in a controlled manner, usually under oxygen or an inert gas. The changes in mass provide information on the thermal stability and the molecular make up of the material. Weight loss can arise from evaporation of residual moisture or solvent but at higher temperatures it results from decomposition of the sample.

2.3.3 Dynamic Mechanical Analysis (DMA)

DMA is a technique which measures the mechanical properties (mechanical modulus or stiffness and damping) of a sample as a function of temperature. It offers a means of measuring molecular mobility within materials and is most commonly used to measure the glass transition temperature of samples but it can also follow changes in mechanical properties [4]. To achieve this, the specimen is subjected to an oscillating stress which follows a sinusoidal waveform:

$$\sigma(t) = \alpha_{max} \sin \omega t$$

Equation 2.3 Equation of the stress a sample is subjected to in DMA

where $\sigma(t)$ is the stress at time t, α_{max} is the maximum stress and ω is the angular frequency of oscillation. Note that $\omega = 2\pi f$ where f is the frequency in Hertz.

DMA measures stiffness and damping which are reported as modulus and tan delta. Because we are applying a sinusoidal force, we can express the modulus as an in-phase component, the storage modulus, and an out of phase component, the loss modulus. The storage modulus, either E' or G', is the measure of the sample's elastic behaviour. The ratio of the loss to the storage is the tan delta and is often called damping. Damping is the dissipation of energy in a material under cyclic load. It is a measure of how well a material can get rid of energy and is reported as the tangent of the phase angle. It tells us how good a material will be at absorbing

energy. It varies with the state of the material, its temperature, and with the frequency.

The glass transition (Tg) can be directly measured via DMA. It is seen as a large drop in the storage modulus when viewed on a log scale against a linear temperature scale, a concurrent peak in the tan delta is also seen. The value reported as the Tg varies with industry with the onset of the E' drop, the peak of the tan delta, and the peak of the E' curve which is the most commonly used.

2.4 Infra-Red Spectroscopy

Many interesting and useful molecular vibrations can be detected and measured in the infra-red region of the electromagnetic spectrum [2]. The most commonly used range of the region is between 4000 cm^{-1} and 600 cm^{-1} (cm^{-1} is the scale used and signifies wavenumber which is the reciprocal of the wavelength measured). Vibrations of individual types of bonds and functional groups occur in particular areas which provide useful structural information on a material. I.R. is a very useful tool in the identification of a great many compounds.

Liquids for analysis are prepared by placing a drop or two of the liquid between plates of sodium chloride (which are transparent through the 4000-600 cm^{-1} region) and then placing the plates in the spectrometer in such a way that the infra-red beam passes straight through the sample. Solid samples are mixed with a hydrocarbon (commonly nujol) to form a thick paste before pressing between the plates.

Alternatively, the sample can be ground with potassium bromide and pressed into a disc using a mould and press before the infra-red beam is passed through the sample. This method eliminates the problems of bands due to the hydrocarbon in the spectrum, although this is not a major problem.

The work described here goes on to use near I.R. which is the region between 5000 cm^{-1} and 4000 cm^{-1}. This is described in a lot more detail in chapter 6.

All FTIR spectra were recorded on a Perkin-Elmer 1710 spectrometer or a Perkin-Elmer Spectrum GX IR spectrometer.

2.5 Mass Spectrometry and MALDI-TOF

Mass spectrometry involves the vaporisation of compounds and the production of ions or charged molecule fragments from the resultant gas phase molecules [2]. These ions or charged fragments are separated by their mass to charge ratio (m/z), detected and recorded. Often, only singly charged ions are produced so the abundance of the ions can be sorted according to m/z and then plotted. The types of ions produced can be predicted to a certain extent so the output provides evidence of a compound's mass and structure. Electrospray ionisation (ESI) mass spectrometry produces a single peak which leads to straightforward confirmation of a sample's mass.

Matrix-assisted laser desorption – time of flight (MALDI-TOF) is a technique used in mass spectrometry which allows for the determination of molecular weights and analysis of very large molecules such as proteins, dendrimers and polymers which are not able to be detected by conventional mass spectrometers as they tend to fragment upon ionisation [5]. In MALDI, the sample is mixed with an excess of an ultraviolet absorbing matrix, commonly a low molecular weight aromatic acid so they can be ionised fairly easily and so that they act as a proton source, again to facilitate ionisation. On irradiation with a focused beam at an appropriate wavelength, the excess matrix sublimes and the embedded analyte molecules are vaporised. Singly protonated ions are formed from the ion-atom collisions, which are then accelerated into the spectrometer.

Mass spectrometry was carried out by the University of St Andrews Mass Spectrometry Service on a Micromass GCT spectrometer and a Micromass LCT spectrometer. MALDI-TOF spectrometry was carried out by the University of St Andrews Biomolecular Mass Spectrometry and Proteomics Service on a Micromass, TofSpec 2E, MALDI-TOF mass spectrometer.

2.6 Industrial Testing

During the course of this work a number of techniques which are used in the coatings/paint industry have been utilised.

Microhardness tests were undertaken on a number of the samples obtained. Tests were undertaken on a Fischerscope® H100C microhardness instrument. This instrument can measure hardness in the range 0.001 – 120,000 N/m^2 with a load range of 0.4 – 1000 mN and an indentation depth of 700 μm. The tests undertaken here used a Vickers diamond indenter and the coatings studied had to be undertaken on glass slides in order for them to be tested. The instrument measures a number of different parameters, the key ones being EIT, Elastic Modulus (GPa), W_t Total Work (nJ), W_e Elastic Work (nJ), W_r Plastic Work (nJ).

Corrosion data was obtained and is described in Chapter 5. The corrosion programmes the samples were subjected to consisted of 1 hour at ambient temperature in salt fog then 1 hour "dry" at 35 ºC. The salt solution is 0.35 % ammonium sulphate, 0.05 % sodium chloride and this was undertaken in an Ascott S450t salt fog chamber. The coatings were applied to grit-blasted steel panels with a small hole drilled into the coating to expose the steel panel. The panel is then placed into the salt fog chamber to observe how the coating performs in terms of minimising the corrosion from the exposed section of steel. After the appropriate time, which in this project was commonly >10 weeks, the panels were removed, photographs taken and studied by comparing against an appropriate standard.

QUV data was obtained and is described in chapter 5. Panels are produced on aluminium sheets and subjected to 4 hours UV at 60 ºC using UVA-340 fluorescent tubes then 4 hours condensation at 45 ºC all in a Q-Panel QUV-SE weatherometer. The panels are placed in the weatherometer which is a cabinet with UV tubes which

has the capability of producing condensation to see how the coatings perform when subjected to the types of conditions they are designed to withstand. In QUV tests the panels are tested for their gloss retention. This is measured by reflectance studies where a laser is shone on the coating and the gloss retention of the coating is measured from the intensity of the reflected signal.

2.7 References

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3. Preparation of Initial Epoxy Species

3.1 Introduction

As mentioned previously, epoxide functionality is used extensively in cure chemistry. The three membered epoxy ring is especially useful in ambient cure systems due to its high reactivity. Here, it was thought that a range of different epoxy-functionalised POSS molecules should be studied.

The first method to be investigated which is described in section 3.2 concentrated on the epoxidation of vinyl functionality. It was thought that this was the most logical starting point as the main starting material was readily available in the laboratory [1]. Also, epoxy functionalisation can be obtained from vinyl groups as shown by Zhang and Laine [2].

Another pathway to epoxy functionalisation is via a simple hydrosilylation reaction. This has already been discussed in section 1.2 of this work and means that epoxy groups can be obtained via a one-step process. Again, the starting material was present in the laboratory [1] which meant that this was a logical route to target.

The final compounds discussed in this section are glycidyl-functionalised. This functionality was targeted as it was thought that this would be more reactive than epoxy functionality meaning that there would be more of a chance that any

compounds obtained would react at ambient conditions. Also, the methodology is exactly the same as that used when synthesising the epoxy derivatives via the hydrosilylation reaction described above.

3.2 Synthesis of intitial epoxy species. Synthesis of octakis(vinyldimethylsiloxyl) octasilsesquioxane and subsequent epoxidation

3.2.1 Introduction

Epoxy-functionalised POSS cubes can be readily synthesized via epoxidation of a vinyl-functionalised POSS molecule [2] therefore, a vinyl POSS molecule was targeted and synthesised. A simple, one step method as demonstrated by Yuchs and Carrado [3] was utilised which involves the treatment of tetramethylammonium silicate with chlorodimethylvinylsilane. This yielded the desired vinyl functionalisation which could be used itself in a curing reaction or, as is reported here, in producing the epoxide group. See figure 3.1.

3.2.2 Experimental

Preparation of octakis(vinyldimethylsiloxyl) octasilsesquioxane (2) [2]

Tetramethylammonium silicate **(1)** (2.0573 g, 1.81 mmol.) was added to a previously stirred solution of hexane (30 cm^3), DMF (60 cm^3) and chlorodimethylvinylsilane (36 cm^3). The mixture was stirred for 90 mins, then cooled in an ice bath for 45 mins,

after which it was hydrolyzed with cold water (300 cm^3). The mixture was then removed from the ice bath until room temperature was attained. The organic layer was separated from the mixture and washed with water (3 x 40 cm^3). The organic layer was concentrated *in vacuo* affording a colourless powder. (0.4762 g, 0.39 mmol, 22.0% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 0.03 (48H, d, Si-(C**H**$_3$)$_2$), 5.85 (24H, m, Si-C**H**-C**H**$_2$). ^{13}C NMR ($CDCl_3$, 300 MHz): δ_C 1.24 (16C, Si-(**C**H$_3$)$_2$), 132.7 (8C, Si-CH-**C**H$_2$), 138.2 (8C, Si-**C**H-CH$_2$).

Full epoxidation of octakis(vinyldimethylsiloxyl) octasilsesquioxane. Preparation of (3) [3]

Octakis(vinyldimethylsiloxyl) octasilsesquioxane (0.0641 g, 0.05 mmol) was dissolved in dichloromethane (5 cm^3) and *m*-chloroperoxybenzoic acid (0.1456 g, 0.84 mmol) was added. The mixture was stirred for 3 days after which the solvent was removed *in vacuo*, leaving a colourless solid. Solid was dissolved in diethyl ether (5 cm^3) and extracted with saturated sodium bicarbonate (4 x 20 cm^3). The diethyl ether was removed *in vacuo* yielding a colourless solid (0.0689 g, 0.05 mmol, 97.3% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 0.06 (48H, m, Si-(C**H**$_3$)$_2$), 2.04 (8H, t, Si-C**H**-CH$_2$), 2.47 (8H, t, Si-CH-C**H**$_2$), 2.72 (8H, t, Si-CH-C**H**$_2$).

3.2.3 Results and Discussion

Tetramethylammonium silicate **(1)** had been prepared previously and was readily available in the laboratory [1]. Reacting this with chlorodimethylvinylsilane in dimethylformamide (DMF) and hexane afforded octakis(vinyldimethylsiloxyl) octasilsesquioxane **(2)** in ca. 30% yield. After a number of attempts the yield was never improved, however such low yielding reactions are not uncommon in POSS synthesis. The purification step, which involves a water wash, was thought to be at fault due to the product being slightly water soluble, leading to the loss of a portion of the product. The reaction did prove to be very reproducible, however with the product being isolated as a colourless powder which meant the subsequent reaction could be attempted.

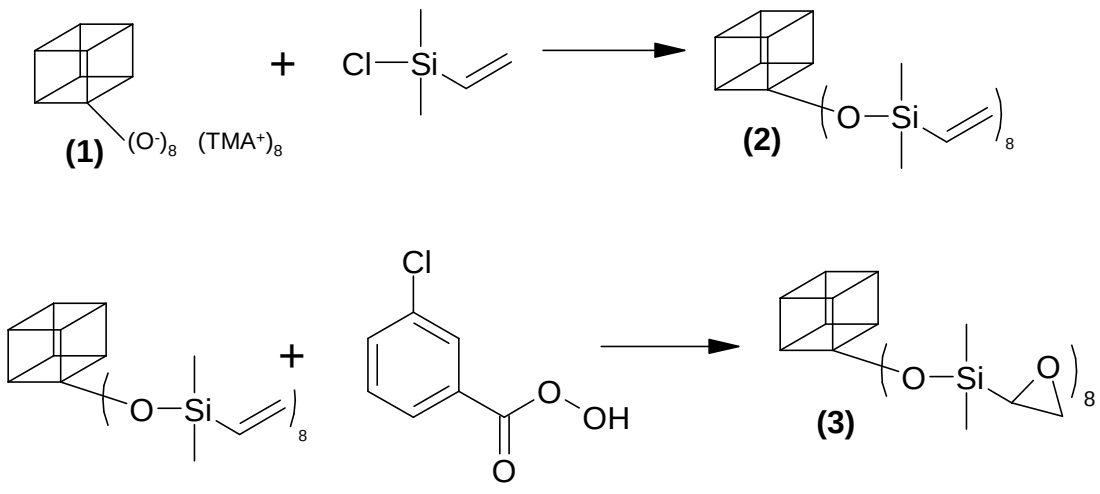

Figure 3.1: Scheme 1

Having successfully prepared **(2)** it was possible to synthesise the epoxy derivative **(3)**. Compound **(2)** was treated with 16 equivalents of *m*-chloroperoxybenzoic acid (*m*-CPBA) in dichloromethane (DCM) for 72 hours. Product purification was not straight-forward. Chlorobenzoic acid is formed in the reaction and separating this from the desired product was not simple. The method in the literature [2] utilized a phosphate buffer of pH 7.5, however all buffers that were used seemed to cause breakdown of the epoxy ring. Eventually, it was seen that the most successful mode of purification was to extract the product four times with a saturated sodium bicarbonate solution, separate and dry it [4]. Compound **(3)** was successfully synthesized, isolated and purified as a colourless powder with yields exceeding 90%.

3.2.4 Conclusions

It has been shown that an epoxy functionalised POSS can be prepared from the vinyl derivative relatively simply and in good yields. This molecule is capable of many further reactions making it an extremely useful material in cure chemistry.

3.3 Epoxy hexyl POSS

3.3.1 Introduction

Another epoxy functionalised POSS compound preparation was attempted. Instead of following a multi-step procedure, which can lead to poor yields and sometimes decomposition of the silsesquioxane [5], it was thought that an epoxy compound

could be reacted with a POSS cube via a simple hydrosilylation reaction. This would mean that the POSS cube would not be subjected to many different reaction conditions, meaning that the POSS cube has an increased chance of survival.

A simple hydrosilylation reaction was attempted which is when an Si-C bond is formed from a C-C double bond. This meant that an epoxide had to be found with a vinyl group present and after a brief literature search [6], a procedure was found where 1,2-epoxy-5-hexene was reacted with compound **(4)**, a compound analogous to **(2)** in order to synthesize compound **(5)**, see scheme 2 (figure 3.2).

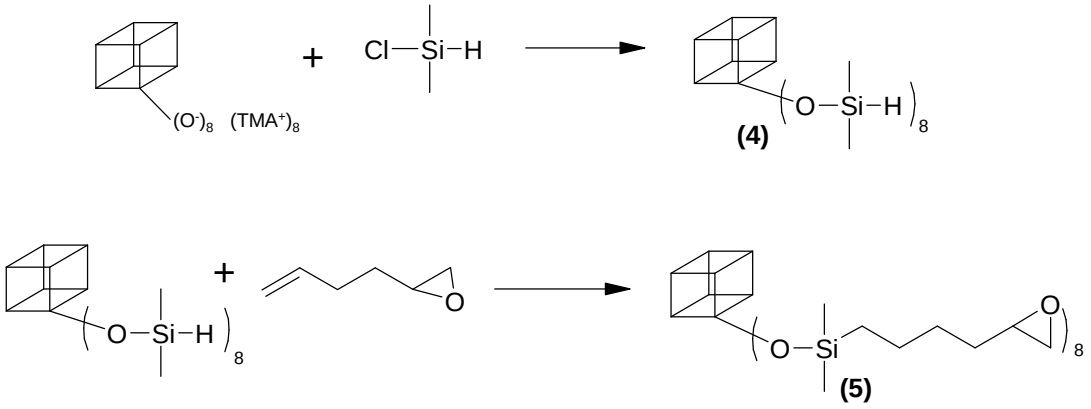

Figure 3.2: Scheme 2

Another epoxy compound, **(6)**, was prepared. It can be seen that this epoxy-POSS compound consists of the epoxy-hexyl group simply grafted to the POSS cube. This can lead to increased yields as the silsesquioxane does not need to be subjected to a number of different manipulations and the chances of reaction success are increased slightly as there are less steps involved. The reaction is shown in scheme 3 (figure 3.3).

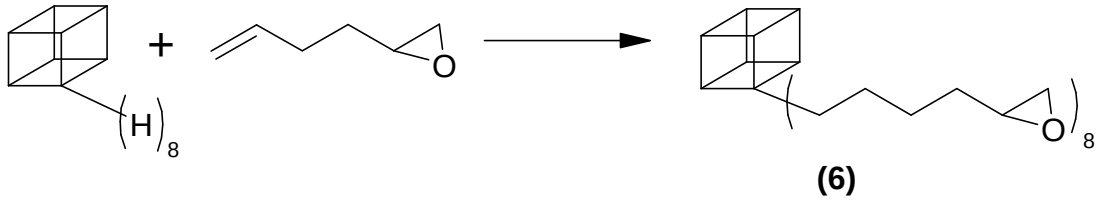

Figure 3.3: Scheme 3

The method used was identical to that found in the literature when preparing **(5)** [6].

3.3.2 Experimental

Preparation of octakis(dimethylsiloxyl) octasilsesquioxane, (4)

Tetramethylammonium silicate **(1)** (0.9839 g, 0.86 mmol.) was added to a previously stirred solution of hexane (20 cm^3), DMF (40 cm^3) and chlorodimethylsilane (20 cm^3). The mixture was stirred for 90 mins, then cooled in an ice bath for 60 mins, after which it was hydrolyzed with cold water (100 cm^3). The mixture was then removed from the ice bath until room temperature was attained. The organic layer was separated from the mixture and washed with water (3 x 20 cm^3). The organic layer was concentrated *in vacuo* affording a colourless powder (0.3547 g, 0.35 mmol, 40.7% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 0.26 (48H, d, Si-(C**H**$_3$)$_2$), 4.74 (8H, sep, Si-(CH$_3$)$_2$-**H**.

Attempted preparation of octakis(dimethylepoxyhexanesiloxyl) octasilsesquioxane, (5) [6]

Octakis(dimethylsiloxyl) octasilsesquioxane, **(4)**, (0.15 g, 0.15 mmol) was dissolved in anhydrous toluene (10 cm^3) and 1,2-epoxy-5-hexene (0.25 cm^3, 2.22 mmol) was added. Pt (dvs), (40 μL) was added with the reaction pot in ice after which the reaction mixture was stirred under reflux for 24 hours. A sparingly soluble colourless solid was yielded. No satisfactory NMR data were obtained.

Preparation of hydride-POSS [7]

To iron (III) chloride (100 g, 0.62 mol) was added concentrated hydrochloric acid (40 mL), methanol (80 mL), hexane (700 mL) and toluene (100 mL). To this mixture was added trichlorosilane (40 mL, 0.40 mol) in hexane (300 mL) drop-wise over a period of 18 hours while the mixture was stirred. The top layer was then removed by separating funnel and dried over K_2CO_3 (28 g) and $CaCl_2$ (20 g). The mixture was filtered and the solution was reduced *in vacuo* to ~40 mL. On cooling a white crystalline product precipitated which was recovered by filtration and washed with hexane. The mother liquor and washings were then reduced *in vacuo* to ~20 mL and a second crop of crystals was collected (yield 22.2%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 4.18 (8H, s, SiH).

The iron (III) chloride layer was recycled and the procedure was repeated as above to yield a white crystalline solid (yield 20.0%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 4.18 (8H, s, SiH).

During the course of this project a significant amount of time was spent attempting to improve the relatively low yield of this reaction, and to scale it up to a level where the absolute amount of materials prepared would be useful for larger scale polymerisation reactions. Unfortunately, in common with many other groups and even a commercial POSS manufacturer there has been little or no success in this endeavour.

Preparation of octakis(epoxyhexane) octasilsesquioxane, (6) [6]

Hydride POSS (0.2134 g, 0.50 mmol) was dissolved in anhydrous toluene (10 cm^3) and 1,2-epoxy-5-hexene (0.95 cm^3, 8.42 mmol) was added. Pt (dvs), (80 μL) was added with the reaction pot in ice after which the mixture was stirred for 3 days. The toluene was removed *in vacuo*, yielding a colourless oil (0.5334 g, 0.44 mmol, 88.0% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 0.56 (16H, t, Si-C**H**$_2$-CH$_2$), 1.51 (48H, m, Si-CH$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$), 2.39 (8H, t, Si-(CH$_2$)$_4$-C**H**), 2.67 (8H, t, Si-(CH$_2$)$_4$-CH-C**H**$_2$), 2.82 (8H, t, Si-(CH$_2$)$_4$-CH-C**H**$_2$) ^{13}C NMR ($CDCl_3$, 300 MHz): δ_C 12.32 (8C, Si-**C**H$_2$-CH$_2$-CH$_2$-CH$_2$), 23.06 (8C, Si-CH$_2$-**C**H$_2$-CH$_2$-CH$_2$), 29.40 (8C, Si-CH$_2$-CH$_2$-**C**H$_2$-CH$_2$), 32.52 (8C, Si-CH$_2$-CH$_2$-CH$_2$-**C**H$_2$), 52.65 (8C, CH$_2$-**C**H-CH$_2$), 66.27 (8C, CH$_2$-CH-**C**H$_2$).

3.3.3 Results and Discussion

Compound **(4)** was synthesized, as shown in scheme 2, using a procedure similar to that which yielded **(2)** [8]. This time the tetramethylammonium silicate was reacted with chlorodimethyl silane which yielded octakis(dimethylsiloxyl) octasilsesquioxane. The product was only ever produced in a yield of ca. 50%. Again, the purification steps seemed to lead to loss of product, as described previously. This was in turn reacted with 1,2-epoxy-5-hexene in the presence of Platinum divinyltetramethyldisiloxane (Pt (dvs)) as a catalyst in anhydrous toluene in an attempt to produce **(5)**. This reaction proved unsuccessful with ^{1}H NMR showing an abundance of unresolved peaks. Time constraints have meant that this reaction has not been repeated.

Compound **(6)** was prepared as shown in scheme 3 (figure 4.3). Hydride POSS had been prepared previously and was readily available in the laboratory [1]. Reacting this with 1,2-epoxy-5-hexene in the presence of Pt (dvs) as a catalyst in anhydrous toluene affords octakis(dimethylsiloxylepoxyhexane) octasilsesquioxane in good yields, ca. >90%. The method involves simply dissolving the hydride POSS in the toluene, adding 10 equivalents of 1,2-epoxy-5-hexene in the presence of the catalyst and stirring for 24 hrs. The product was isolated as a colourless oil and ^{1}H NMR verified that the product had been synthesized successfully. It should be noted that the first three times the reaction was attempted, the catalyst was removed by passing the product through a silica column. This led to yields of ca. 40% due to the fact that epoxides are too reactive to survive a column, however after consultation with

scientists at the industrial sponsor [9] it was decided that leaving the catalyst in the product should not affect any results at this time, meaning that yields were greatly improved.

3.3.4 Conclusions

It has been demonstrated that an epoxy functionalised POSS can be prepared from hydride POSS and the corresponding epoxide. This molecule is capable of further reactions making it a very useful compound in cure chemistry. There is also a lot of potential with this reaction, as it seems that the epoxide molecule could be varied in terms of the length of the alkyl chain. The ease with which this epoxy POSS was prepared may lead to a whole range of other POSS molecules being made with subtly different epoxide groups.

Compound **(5)** was never isolated and purified satisfactorily. However, up until now there has not been the need to re-visit this reaction because other epoxy functionalised POSS molecules have been pursued.

A great deal of time as spent trying to scale up the synthesis of the H-POSS, even to the point of trying to design new pieces of equipment to facilitate the slow addition of the silane to the reaction mixture. This was unsuccessful, and the limitations placed on the available starting materials because of this reaction clearly limit the applicability of H-POSS in commercial and even large scale academic research and development.

3.4 Glycidyl POSS

3.4.1 Introduction

Two further epoxy functionalised POSS molecules were targeted as shown in scheme 4 (figure 3.4). It was thought that a glycidyl functionalised POSS would be even more reactive than an epoxide group so attempts were made to prepare compounds **(7)** and **(8)**. Compound 8 (Glycidyl-POSS) is discussed and investigated in a lot more detail in chapter 5 of this work.

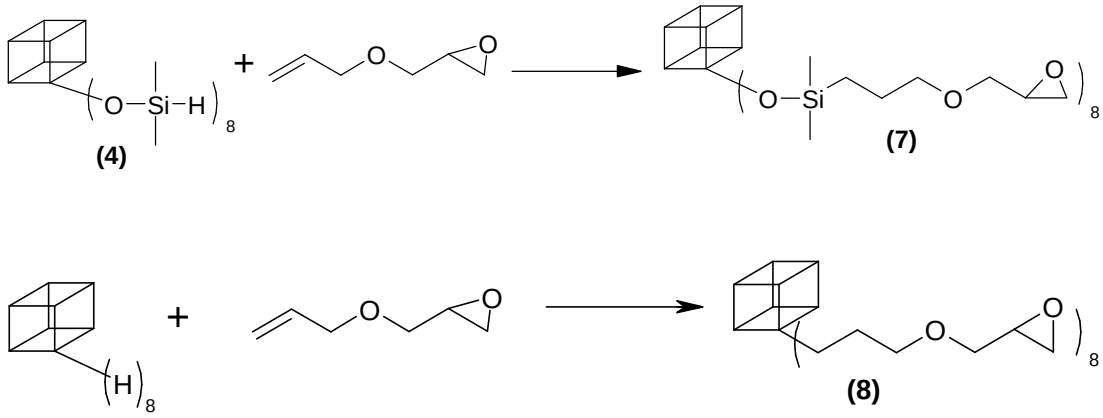

Figure 3.4: Scheme 4

These compounds were attempted to be synthesized in exactly the same way as **(5)** and **(6)** only using allyl glycidyl ether (AGE) instead of epoxy-5-hexene [6]. The hydrosilylation reaction should take place in exactly the same way as before with a Si-C bond being created from the double bond.

3.4.2 Experimental

Preparation of octakis(dimethylglycidylsiloxyl) octasilsesquioxane (7) [6]

Octakis(dimethylsiloxyl) octasilsesquioxane, **(4)**, (0.08 g, 0.08 mmol) was dissolved in anhydrous toluene (5 cm^3). Allyl glycidyl ether (0.1 cm^3, 0.84 mmol) was added and the reaction mixture was stirred. Pt (dvs), (40 μL) was added with the reaction flask in ice after which the reaction was stirred under reflux for 24 hours. The toluene was removed *in vacuo*, yielding a dark brown oil (0.16 g, 0.08 mmol, 99.1% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 0.46 (16H, m, O-Si$(CH_3)_2$-C**H**$_2$), 1.46 (48H, m, O-Si-(C**H**$_3)_2$), 2.47 (8H, m, O-CH_2-C**H**-CH_2), 2.65 (8H, m, O-CH_2-CH-C**H**$_2$), 3.01 (8H, m, O-CH_2-CH-C**H**$_2$), 3.29 (16H, m, O-Si$(CH_3)_2$-CH_2-C**H**$_2$), 3.57 (16H, m, O-Si$(CH_3)_2$-CH_2-CH_2-C**H**$_2$), 3.90 (16H, m, O-Si$(CH_3)_2$-CH_2-CH_2-CH_2-C**H**$_2$)

Preparation of octakis(glycidyl) octasilsesquioxane (8) [6]

Hydride POSS (0.3397 g, 0.80 mmol) was dissolved in anhydrous toluene (15 cm^3) and allyl glycidyl ether (1.00 cm^3, 8.40 mmol) was added. Pt (dvs), (100 μL) was added with the reaction pot in ice after which the mixture was stirred for 5 days. The toluene was removed *in vacuo*, yielding a brown oil (1.0758 g, 0.80 mmol, 99.9% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 0.60 (16H, m, Si-C**H**$_2$-CH_2-CH_2-O), 1.62 (16H, m, Si-CH_2-C**H**$_2$-CH_2-O), 2.56 (8H, m, O-CH_2-C**H**), 2.74 (8H, m, O-CH_2-CH-

C**H**$_2$), 3.09 (8H, m, Si-CH$_2$-CH-C**H**$_2$), 3.40 (16H, m, Si-CH$_2$-CH$_2$-C**H**$_2$-O), 3.65 (16H, m, O-C**H**$_2$-CH).

3.4.3 Results and Discussion

Compounds **(7)** and **(8)** were successfully prepared by following the procedure described above only with AGE instead of the epoxy-5-hexene. The reaction proved very reproducible with yields in excess of 90%. Both products were isolated as brown oils and the structures were verified by ^{1}H NMR.

3.4.4 Conclusions

It has been shown that a glycidyl functionalised POSS can be prepared relatively simply and in good yields. It is hoped that this compound will be even more reactive than the epoxy POSS compounds. This would mean that it is more likely to take part in curing reactions at room temperature which is the main aim of this part of the project.

3.5 Overall Conclusions

The work undertaken here has shown that an epoxy functionalised POSS can be prepared from a vinyl derivative relatively simply and in good yields. This molecule is capable of many further reactions making it an extremely useful material in cure chemistry.

It has also been shown that an epoxy functionalised POSS can be prepared from hydride POSS and the corresponding epoxide. This molecule is capable of further reactions making it a very useful compound in cure chemistry. There is also a lot of potential with this reaction because the epoxy functionality can be varied in terms of the length of the alkyl chain. The ease with which this epoxy POSS was prepared could lead to a whole range of different POSS molecules being designed and synthesised with subtly different epoxide groups.

Compound **(5)** was never isolated and purified, however, up until now there has not been the need to re-visit this reaction because other epoxy functionalised POSS molecules have been pursued.

As already mentioned a great deal of time was spent trying to scale up the synthesis of the H-POSS which placed limitations on the available starting materials. This meant there were problems with fully investigating the associated reactions.

It has also been shown that a glycidyl functionalised POSS can be prepared relatively simply and in good yields. This compound was targeted as it is hoped that this compound will be even more reactive than the epoxy POSS compounds. This would mean that it is more likely to take part in curing reactions at room temperature which is the main aim of this part of the project and it was hoped that this material could be an important one in the context of this work going forward.

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4. Initial Polymerisation Reactions

4.1 Introduction

The molecules which have been synthesised and discussed in chapter 3 have been designed and isolated to take part in polymerisation reactions, therefore the next step is to see if these molecules can take part in a simple cure. This forms a basic test as for the suitability of the reactions for taking further and looking at whether they synthesized molecules are promising for further polymerisation studies.

If the POSS compounds already discussed can take place in simple cure reactions then the hope is that some of the properties discussed in the introduction such as an increase in thermal stability [1], an increase in abrasion resistance [2] and increases in oxidation resistance [3] could be added to any films being produced here.

Curing techniques commonly use epoxy functionalisation which is reacted with an amine curing agent [4]. The reactivity of the three-membered ring is enough to react with the amine at ambient temperatures. Epoxy functionality has been targeted thus far so it was concluded that this line of work should be investigated.

Initial attempts were made at the curing reactions and are discussed below. The results to these initial reactions meant that a certain amount of investigation was undertaken in order to study the processes at work. The systems were simplified a lot

to see if the mechanics of the reactions could be understood in a lot more detail. It was not until after these initial modeling reactions had been attempted that it became clear that, in established curing reactions involving epoxide and amine groups, the concentration of reactants has to be controlled in such a way that an amine proton is present for each epoxy group present.

The main aim of this section of work was to see if the compounds synthesised and isolated in Chapter 3 could not only take part in simple polymerisation reactions but also to see if said reactions could take place at ambient temperatures.

The structures of any solid polymers obtained here were also investigated. ^{29}Si MAS and ^{13}C MAS solid state NMR was utilised firstly, to see if the POSS cube survives the polymerisation reaction and is intact as an integral part of the polymer and secondly to try and investigate the structure of the polymers.

4.2 Experimental

4.2.1 General procedure for model polymerisation reactions

Epoxy-5-hexene (1 mL, 0.99 g, 9.24 mmol) was added to propan-2-ol (20 cm^3) and the appropriate amount of amine was added. The mixture was stirred and heated to reflux for typically 10 hours. All products were isolated as colourless solids. Electrospray mass spectrometry was used as the initial characterization technique to screen the model reactions for successful polymerization.

Epoxy-5-hexene + 3 equivalents of benzylamine

MS (ESI) *m/z* (relative intensity): 206 (100), 207 (2)

Epoxy-5-hexene + 1/2 equivalent of benzylamine

MS (ESI) *m/z* (relative intensity): 206 (21), 304 (11), 326 (100)

Epoxy-5-hexene + 3 equivalents of m-xylylenediamine (m-XDA)

dr 29: MS (ESI) *m/z* (relative intensity): 120 (100), 235 (78)

4.2.2 General procedure for polymerisation reactions

Epoxy functionalised POSS (0.5 g) was dropped onto a microscope slide and the amine (2 equivalents) was added. The reaction mixture was stirred using a needle

and then left until polymerisation had occurred, typically within 8 hours. Products were crushed using a mortar and pestle for analysis by solid state NMR.

4.3 Results and Discussion

Initially, three reactions were attempted as shown in scheme 4.1 (figure 4.1).

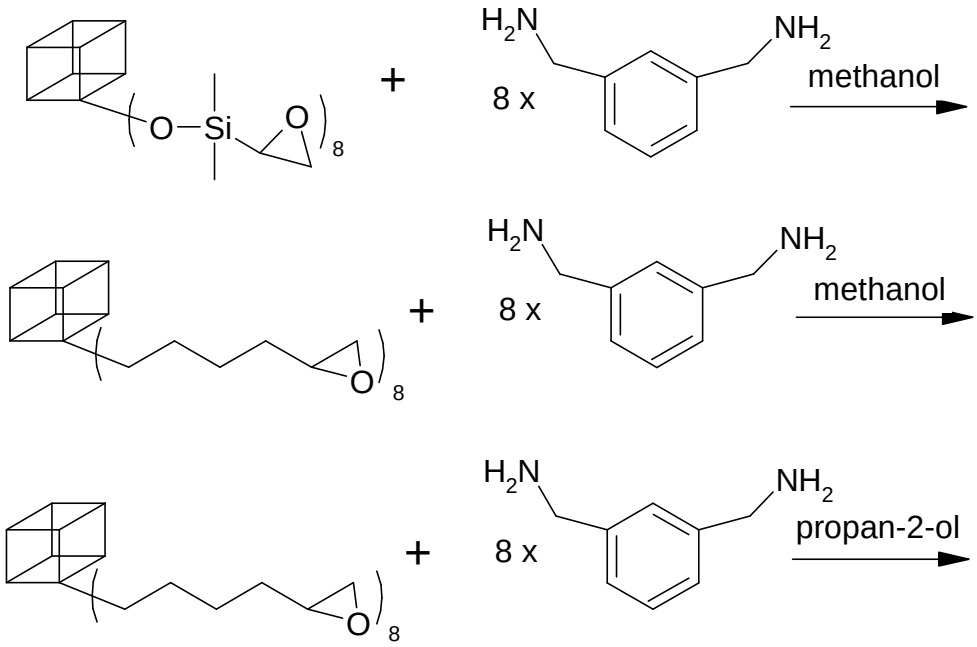

Figure 4.1 Scheme 4.1

In each case, the POSS compounds were dissolved in the solvent and the amine was added to the stirring solution. Methanol and propan-2-ol were used as they are a common solvent in POSS chemistry. The reactions were left to run for ten days. Very little was yielded from these reactions and when the solvent was removed insoluble, colourless powders remained. The products were never fully examined as

it was thought that understanding the processes at work should be investigated. This meant carrying out the same reactions on much simpler compounds, i.e. reacting epoxy-5-hexene with the amine. It was hoped that this would mean that characterising any products would be made simpler since discrete molecules would be yielded instead of large polymers.

Therefore, the following reaction was undertaken:

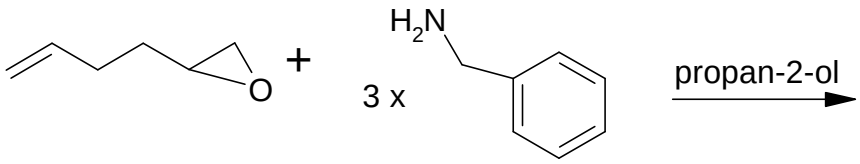

Figure 4.2 Epoxy-5-hexene + 3 equivalents of benzylamine

As can be seen, a mono-functional primary amine (benzylamine) was tested. This was used in order to make things a little simpler which would lead to products being a lot more straight forward to interpret. Three equivalents of the amine were added because it was important to examine the processes at work when excess amine was added. ^{1}H NMR was inconclusive with broad, unresolved peaks present, showing that the product was very immobile. Obviously, another technique had to be employed to identify the product and electrospray ionisation mass spectrometry (ESI MS) was used. This proved much more successful and showed that the following compound had been synthesised:

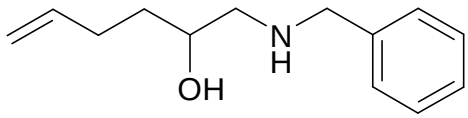

Figure 4.3 Product yielded from epoxy-5-hexene + benzylamine

This product was produced when excess amine was used, so it was thought that the next step should be to control the stoichiometry of the reaction, reacting one amine proton with each epoxy group. The following reaction was undertaken:

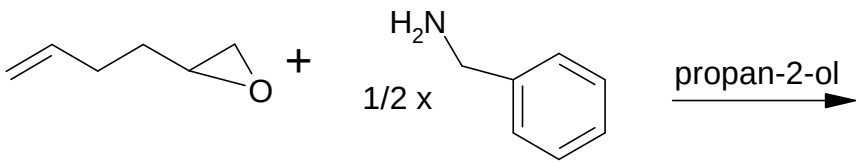

Figure 4.4 Epoxy-5-hexene + 1/2 equivalent of benzylamine

Once again, ^{1}H NMR did not provide any useful information (including variable temperature experiments [5]) so ESI MS was utilised. The results showed that a mixture of two products was present as shown below:

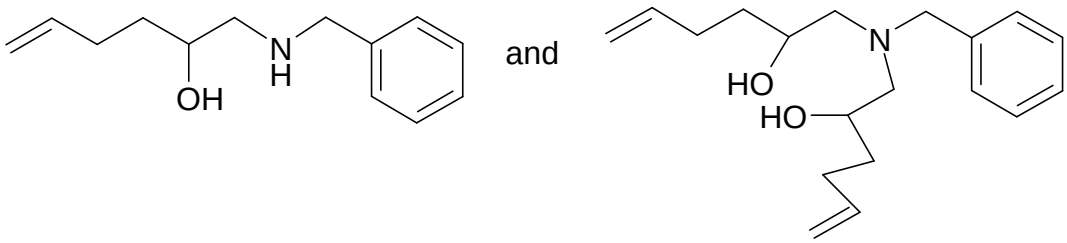

Figure 4.5 Products from epoxy-5-hexene + 1/2 equivalent of benzylamine

^{1}H NMR proved inconclusive because the products have very similar spectra and distinguishing them was far from straight-forward.

From this result it looked as though when the stoichiometry of the reaction is controlled, then polymerisation is more likely to take place. This may be down to the fact that when there is more amine present, there is less chance of an amine group reacting with two epoxide rings simply because the control is not present in the reaction mixture. What is likely to happen is that having a higher concentration of amine groups present in the reaction will mean that one amine group is far less likely to react with two epoxy groups. When the amount of amine is controlled there is a much larger chance of the amine group reacting with two epoxy groups.

This theory becomes much more important when a di-amine is used. If an excess is used, then there is much less chance of polymerisation taking place because when the first amine proton reacts with an epoxide ring, there is much less chance of the other amine group coming within close proximity of another epoxide, meaning that only one of the four amine protons will have reacted.

With this in mind, the following reaction was undertaken to establish what actually happens when excess di-amine is used:

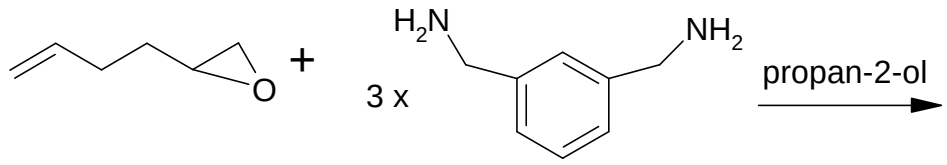

Figure 4.6 Epoxy-5-hexene + 3 equivalents of m-XDA

Once again, ^{1}H NMR proved inconclusive, however, ESI MS showed that the following had been prepared:

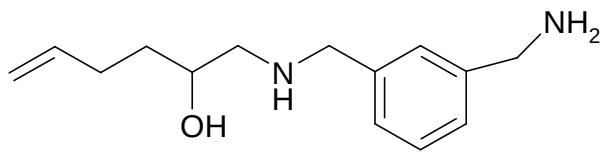

Figure 4.7 Product yielded from epoxy-5-hexene + 3 equivalents of m-XDA

This result showed that if the epoxide is reacted with excess amine, then only one of the amine protons is likely to react. Therefore, if a polymer is to be formed using the same di-amine then the stoichiometry has to be controlled, with an amine proton in reaction for each epoxy group.

As a result of the model polymerisation reactions with no POSS core present, the next step was to go back to the original cure reactions and apply what was observed. Therefore the following two reactions were attempted:

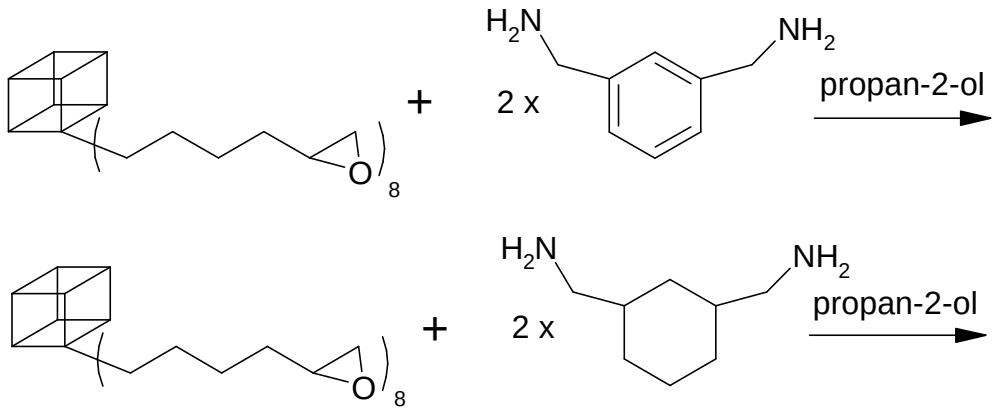

Figure 4.8 Polymerisation reactions with epoxy-hexyl POSS + m-XDA and epoxy-hexyl POSS + cyclohexanebis(methylamine)

After a few hours, solids were apparent in both reaction mixtures. It was noted that there was far too much solvent in the reaction pot meaning that the concentration of the reactants could be increased by removing some solvent. Solvent was removed from both reactions, leaving ca. 2mL. Overnight, both reaction mixtures had formed a gel. At this point it was thought that the reactions should be carried out without a solvent as it was hindering polymerisation.

This meant that the same reaction was undertaken only this time with the amine added to the epoxy-POSS compound neat, as shown below:

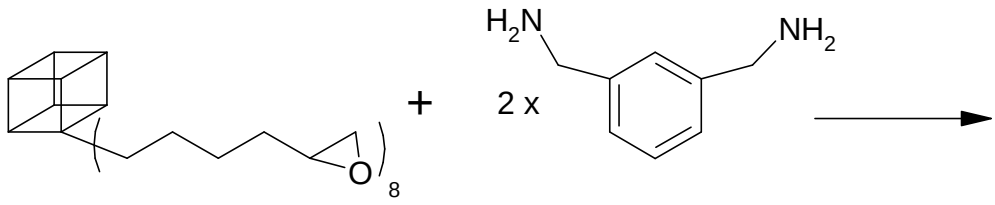

Figure 4.9 Epoxy-hexyl POSS + 2 equivalents of m-XDA. Reaction attempted neat.

The reaction was left overnight, after which time the reaction mixture had solidified and a polymer had formed. The solid formed was extremely brittle and “glassy” like. It was crushed up for analysis by solid state NMR.

Three other polymerisation reactions were undertaken as shown below in figure 4.10:

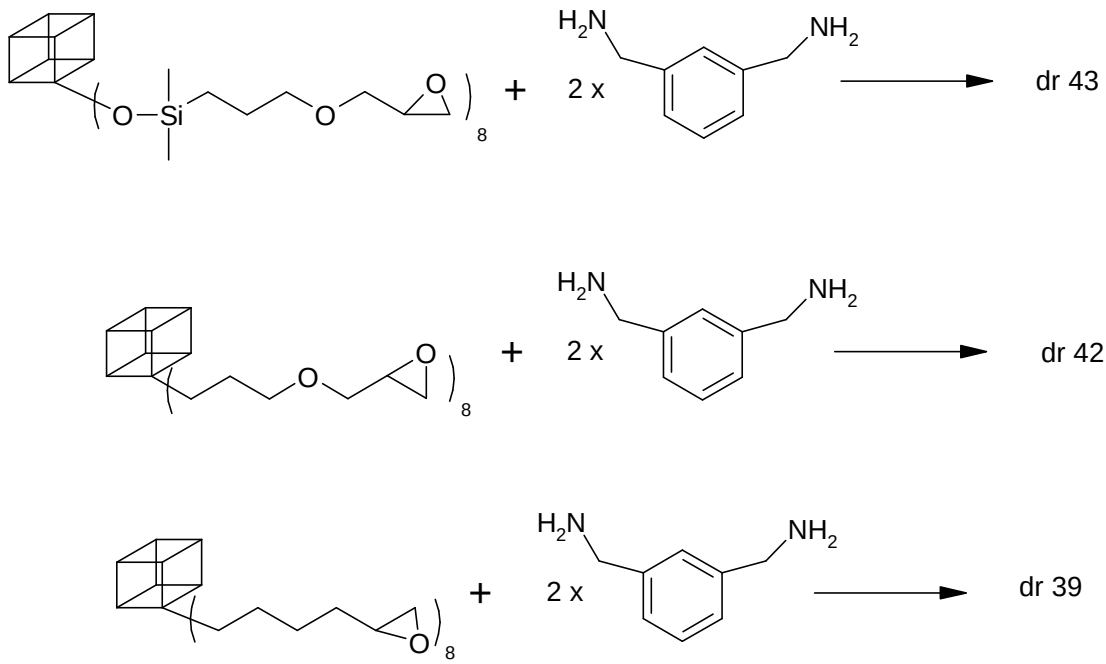

Figure 4.10 Three polymerisation reactions attempted neat on a microscope slide

Each of these reactions was carried out on a microscope slide covered in Teflon tape so the polymer could be removed simply. All three reactions proved successful with polymers formed within hours of the amine being added. It could be seen that the glycidyl POSS compounds were by far the most reactive as a polymer was formed within ca. 2-3 hours.

Figure 4.11 shows the ^{29}Si MAS solid state NMR data obtained from the three reactions outlined in figure 4.10.

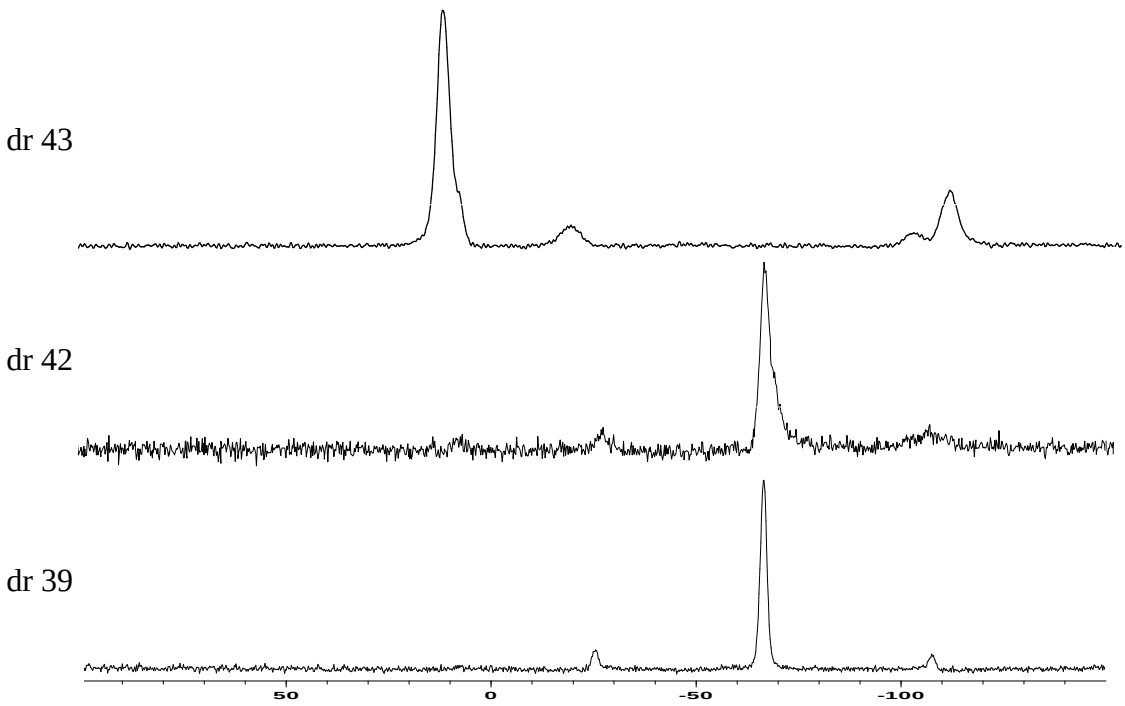

Figure 4.11 ^{29}Si MAS solid state NMR for compounds dr 39, dr42 and dr 43

^{29}Si silsesquioxane peaks appear in the range -60-70 ppm [6]. The spectra obtained for dr 39 and dr 42 show one, well resolved peak which corresponds to the POSS

cube. This shows that the silsesquioxane is intact and proves that the POSS core survives the polymerisation reactions.

The spectrum obtained for dr 43 shows 2 silicon peaks as expected. The peak at 8 ppm corresponds to the Si which has the two methyl groups attached and the peak at -110 ppm corresponds to the SiO_4 group which is present. These values match up with literature values [6] and shows that the silsesquioxane survives the polymerisation.

^{13}C solid state NMR data was obtained and is shown below (figure 4.12).

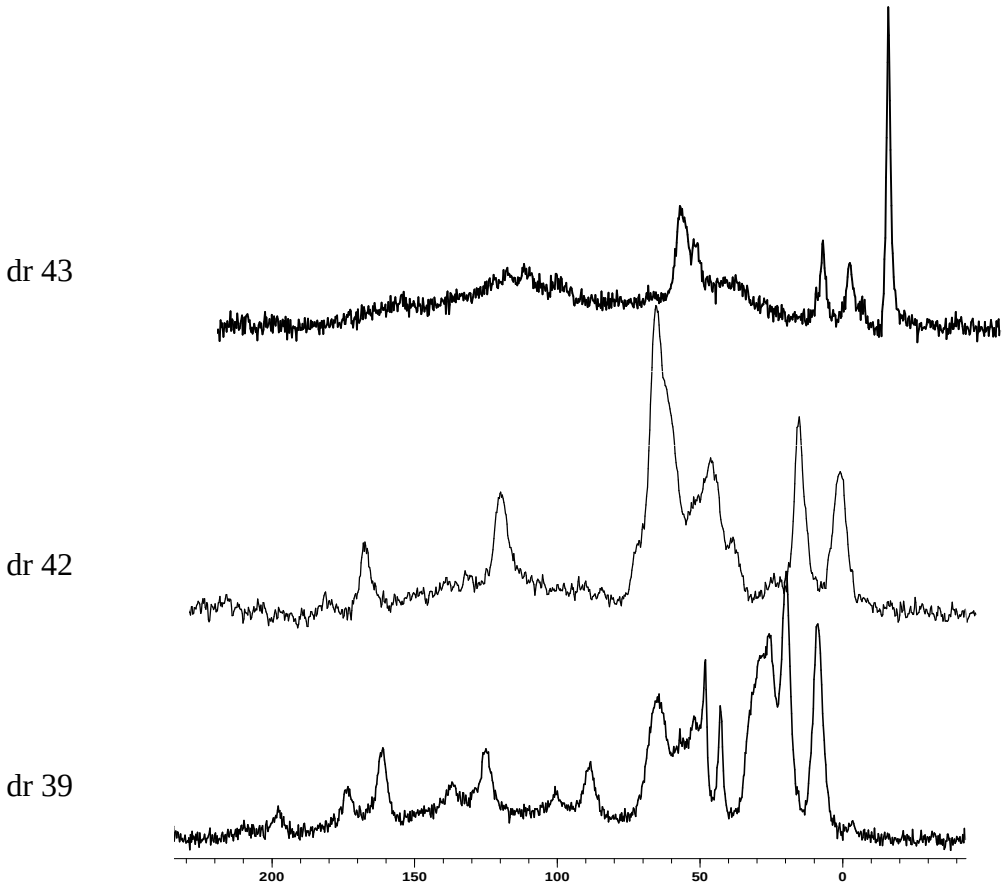

Figure 4.12 ^{13}C MAS solid state NMR for compounds dr 39, dr42 and dr 43

As can be seen, the ^{13}C data obtained is a lot more complicated than the ^{29}Si data however some assignments can be made. Typically, CH_2 groups appear in the range 0-10 ppm [6] and it can be seen that there are multiple CH_2 signals. This would be expected as there will be many different CH_2 environments present due to some of the functional groups not reacting, some of them reacting with one amine proton and some of the epoxides reacting with two amine protons. In many cases the CH_2 groups will be indistinguishable by solid state NMR techniques.

Aromatic carbons reside in the range of 105-130 ppm [6]. It can be seen that each polymer definitely has aromatic carbons present, showing that the amine is part of the polymer system.

The solid state NMR experiments have therefore proved that the POSS species remains intact during the polymerisation reactions and that the solids also incorporate the aromatic amine functionality.

4.4 Conclusions

It has been shown that POSS species, namely compounds 6, 7 and 8 can be used in ambient cure polymerisations. Each molecule formed a solid polymer when reacted with an amine which signifies that these types of species can be incorporated into established coatings chemistry as they behave in the desired fashion. Crucially, the silsesquioxane cage is intact as verified by ^{29}Si solid state NMR. At this stage it

appears that the species prepared so far may be of suitable reactivity for coatings applications.

Also, a much better understanding of the processes which are involved in these types of polymerisation reactions has been achieved by simplifying the reactions that were studied. This meant that when the appropriate polymerisation reactions were attempted in more detail, a lot of knowledge had already been gained about the systems at work.

It was shown that when an amine is reacted with an epoxy functionalised compound, the amount of amine used has to be carefully calculated with one amine proton present for each epoxy ring in the system. If an excess of amine is used then polymerisation is less likely to take place.

A number of polymerisation reactions have been undertaken and the knowledge gleaned from these is extremely important to other parts of this work. The ^{29}Si solid state NMR data shows that the POSS cube is still intact however the ^{13}C data shows that it will be far from straightforward to identify exactly all that has gone on in the cure. Other techniques will have to be employed to understand these polymers fully and it may be that the processes at work may not be observed at all.

4.5 References

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5. Synthesis and Use of Glycidyl Species in Polymerisation Reactions

5.1 Introduction

As described earlier, POSS molecules can be manipulated in such a way that porous polymers can be prepared. They can be used in a number of areas of chemistry such as catalysis [1], zeolite-type chemistry [2], designing frameworks and many more. The design and synthesis of these molecules can be specifically tailored to suit a number of different criteria with the main ones being the length and rigidity of the organic linkers. Obviously, this affects the porosity of the polymer but at the same time it can affect the reactivity of the molecule which, in turn affects the polymer obtained.

It should be noted here that coatings that cure at ambient temperatures are desirable. This means that when a cure is undertaken it can occur at room temperature and does not require any extra energy in order for the curing reaction to take place. This means that the target coatings can be obtained by simply mixing the reactants and leaving them to produce a polymer. Obviously this leads to not having to cure all of the mixtures by using any extra energy i.e. an oven and when used in a more industrial sense it would mean that coatings could be produced with much less effort and energy.

A glycidyl functionalised molecule is desirable for this as it can react at ambient temperatures and it is relatively easy to prepare, making it an ideal candidate for this type of work [3]. Due to its reactivity it is hoped that if the original molecule can be prepared in 100 % purity then all sites will react and produce a highly cross-linked polymer.

By far the most common way of incorporating POSS into coatings systems is by “hanging” them off a backbone which is made up of a more recognisable polymer chain. Incorporating POSS in this way is commonly referred to as “pendant POSS” [4].

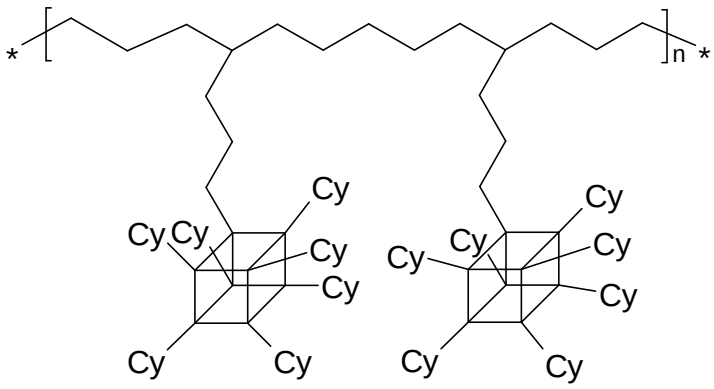


Figure 5.1 Simple schematic of “pendant POSS” incorporated onto a polymer backbone

As can be seen the POSS molecule only needs one reactive site and the other seven can be made up by any non-reactive organic group, commonly cyclohexyl or cyclopentyl.

The addition of POSS to coatings systems is based overwhelmingly on pendant POSS. This is because synthesis of these T_7 materials is a lot simpler than the more complicated T_8 species where achieving 100 % conversion can be extremely difficult. There are a number of problems associated with the octafunctional species and these include trapping solvent in the silsesquioxane clusters themselves, trapping solvent between the functional groups of neighbouring POSS cubes and not achieving full conversion due to steric hindrance from larger organic arms attached to the POSS.

Scaling up the synthesis of T_8 molecules is extremely difficult, particularly the H-POSS and being able to synthesise large amounts ~ 20 g is both time consuming and labour intensive. On the other hand, synthesis of T_7 species which are used widely in coatings has been successfully scaled up and many of these molecules can be produced simply or purchased relatively cheaply [5].

The benefits of these pendant POSS systems have been well documented and are seen to increase thermal stability [6], abrasion properties [7] and impact properties [8] of the polymeric systems they are incorporated into. The basic idea of this is to see what adding the POSS cube in such a simple way can add to the system. Here, the aim is to incorporate POSS in such a way that it is a fundamental part of the polymer matrix. This means that octafunctionalised POSS molecules have to be designed and synthesised and then reacted with curing agents, commonly amines [9], in the hope that polymerisation will take place.

In this chapter the material which was studied in more detail was a glycidyl functionalised POSS (see figure 5.2) which has already been discussed in chapter 3. For the remainder of this chapter, this material will be referred to as glycidyl-POSS.

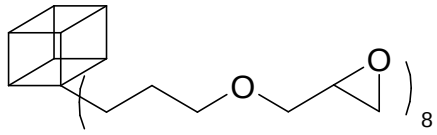


Figure 5.2 Depiction of glycidyl-POSS (Please note the Si_8O_{12} core is shown as a cube with only one organic "arm" for clarity)

Given the partial success of the model curing reactions described in Chapter 4, it was thought that glycidyl-POSS would be even more highly reactive due to the electron donating properties of the oxygen and would hopefully react or cure at ambient temperatures. The choice of glycidyl POSS was also made in the knowledge that compounds of similar reactive groups (e.g. see DGEBA below) are already well known in the coatings industry and therefore one would expect it to be possible to use similar chemistry on the external surface of the POSS. It should be noted at this point that the material used was with the glycidyl group bonded directly to the POSS cube. There was some experimentation undertaken with an $OSiMe_2$ "spacer" between the POSS cube and the glycidyl group (see figure 5.3) but the decision was made not to progress with this idea as it was thought that the more flexible glycidyl group stood more of a chance of successfully curing.

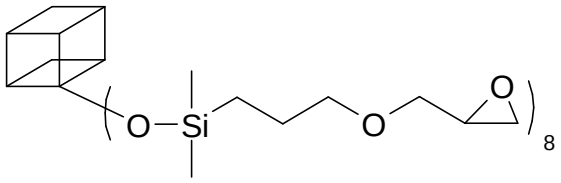
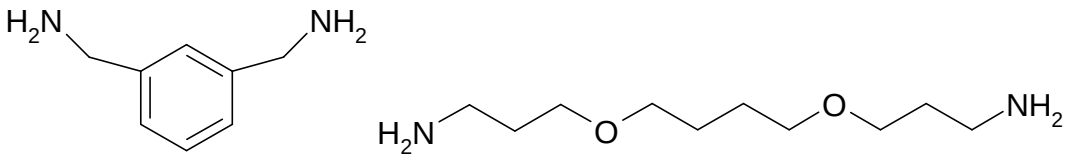


Figure 5.3 Depiction of glycidyl-POSS with the $OSiMe_2$ "spacer" between the POSS core and the glycidyl group (Please note the Si_8O_{12} core is shown as a cube with only one organic "arm" for clarity)

Over the course of this chapter, the glycidyl-POSS was reacted with two different amines, namely m-xylylenediamine (m-XDA) and 4,9-Dioxa-1,12-dodecane-diamine (DODA) as shown in figure 5.4.



m-XDA DODA

Figure 5.4 The amines used in this chapter

These amines are used extensively in the coatings industry and it was hoped that the silsesquioxane systems would behave in the same way as other, more recognised coatings systems. It was thought that a comparator should be sought to see if any changes observed are brought about by the POSS or just by having an inorganic incorporated into the coating. Obviously the POSS cube adds a 3-D nature to the

system and it was thought that undertaking the same reactions with a cyclic molecule would show the effects of the cube. The amines were reacted with a glycidyl cyclic siloxane compound (tetra glycidyl methyl cyclotetrasiloxane) as can be seen in figure 5.5.

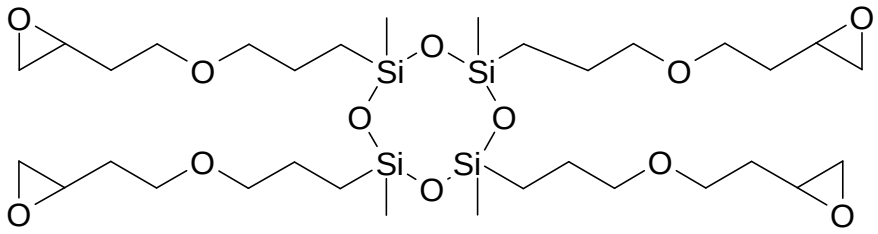


Figure 5.5 Tetramethylglycidyl cyclotetrasiloxane

A linear comparator was sought also and di-glycidyl ether of Bisphenol A (DGEBA) was used as shown in figure 5.6.

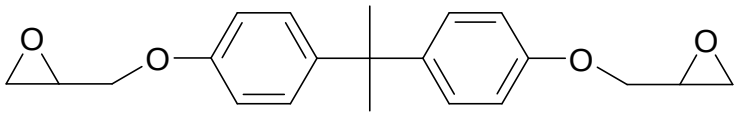


Figure 5.6 DGEBA

This is a material used extensively in the coatings industry and it was hoped that a comparison would help show the effects of the POSS cube and the siloxane ring. Obviously there is a difference in the functionality and molecular mass etc between

the three comparisons but this would be factored in when observing any changes observed.

Not only were the individual epoxy compounds investigated but it was thought that it would be worthwhile to study the effects of blending the different epoxides. A series of different blends were set up and reacted with the amines to see what a mixture of, say siloxane and silsesquioxane adds to any polymers obtained.

5.2 Experimental

5.2.1 Preparation of hydride-POSS [10]

See experimental on p 59.

5.2.2 Preparation of glycidyl-POSS [11]

See experimental on p 64.

5.2.3 Polymerisation (curing) reactions

5.2.3.1 General

All curing reactions were undertaken on glass slides coated with Teflon tape to aid removing the solid polymer. Each epoxy group was reacted with an amine proton,

therefore when the 8 functional silsesquioxane was reacted, 2 equivalents of the amine were added, when the cyclic siloxane was reacted, 1 equivalent of the amine was added and when DGEBA was used it required ½ an equivalent of the amine.

In all cases, the two reactants were mixed in a sample vial, left to blend for ~5 mins, and "drawn down" on the glass slide using a 400 μm bar. All polymerisation reactions yielded a solid within 12 hours.

5.2.3.2 Example of curing reaction with a silsesquioxane. Glycidyl-POSS + m-xylylenediamine

Glycidyl-POSS (4.0103 g, 2.9975 mmol.) was measured into a sample vial. m-XDA (0.8212 g, 6.0294 mmol.) was added and the mixture was stirred for 5 minutes. The mixture was then spread out or "drawn down" onto a Teflon-coated glass slide with a 400 μm bar. A solid polymer was yielded within 8 hours. The solid was removed from the slide using a microspatula.

5.2.3.3 Example of curing reaction with a cyclic siloxane. Cyclic-glycidyl siloxane + m-xylylenediamine

Cyclic-glycidyl siloxane (3.5009 g, 5.0263 mmol.) was measured into a sample vial. m-XDA (0.6849 g, 5.0286 mmol.) was added and the mixture was stirred for 5 minutes. The mixture was then "drawn down" onto a Teflon-coated glass slide with a

400 μm bar. A solid polymer was yielded within 8 hours. The solid was removed from the slide using a microspatula.

5.2.3.4 Example of curing reaction with DGEBA. DGEBA + m-xylylenediamine

DGEBA (4.0129 g, 11.803 mmol.) was measured into a sample vial and heated to melting using a heat gun. m-XDA (0.8057 g, 5.9156 mmol.) was added and the mixture was stirred for 5 minutes. The mixture was then “drawn down” onto a Teflon-coated glass slide with a 400 μm bar. A solid polymer was yielded within 8 hours. The solid was removed from the slide using a microspatula.

5.2.3.5 Example of a curing reaction with a blend. Reaction of 70 % cyclic-glycidyl siloxane, 30% DGEBA + m-xylylenediamine

Cyclic-glycidyl siloxane (2.4513 g, 3.5194 mmol.) was measured into a sample vial. DGEBA (1.5016 g, 3.0929 mmol.) were measured into a sample vial and heated to melting using a heat gun. The two were mixed together and stirred for 5 minutes. m-XDA (0.6871 g, 5.0448 mmol.) was added to the mixture and stirred for 5 minutes. The mixture was then “drawn down” onto a Teflon-coated glass slide with a 400 μm bar. A solid polymer was formed within 8 hours. The solid was removed from the slide using a microspatula.

5.3 Results and Discussion

The strategy was to build up a data set for two different amines with a silsesquioxane epoxy, which obviously has the three-dimensional aspect, a cyclic epoxy, which only possesses the two-dimensional ring and a linear epoxy (DGEBA). This means that the POSS system can be directly compared with other coatings systems and seeing what, if anything, the POSS adds to the properties of the resulting polymers. The first target molecule was the glycidyl functionalised POSS then the cyclic-glycidyl siloxane and the corresponding reactions with the two amines.

5.3.1 Synthesis and isolation of Glycidyl-POSS

A method adapted from the reaction between octahydridosilsesquioxane (H-POSS) and 1,2-epoxy-5-hexene from Huang *et al* [11] was utilized (scheme 1, figure 5.3.1) using allyl glycidyl ether (AGE) in place of the 1,2-epoxy-5-hexene as discussed in section 3.4 of chapter 3 of this work. It was anticipated that the hydrosilylation reaction would proceed in the same manner and the molecule yielded would react with established amines in the coatings industry. It was thought that the hydrosilylation may take place at room temperature so at first it was undertaken at ambient and after three days of stirring in the presence of Karstedt's catalyst the ^{1}H NMR of the product showed there was no signal from the H-POSS. Therefore, as far as could be deduced from ^{1}H NMR, 100% conversion to the octaglycidylsilsesquioxane had been achieved.

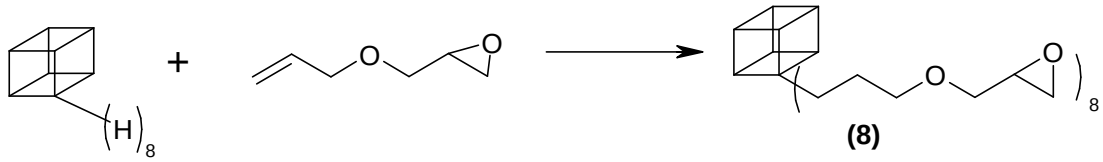


Figure 5.3.1 Scheme 1

The product was reacted with m-xylylenediamine (m-XDA) in order to see if it was compatible with the amine. Epoxies are not always compatible with amines. When this is the case, upon mixing a white “milky” substance is formed and polymerisation does not take place. This can be down to a number of things but the most common reason for this happening is oxidation occurring at the surface of the mixture. When the reactants are mixed the surface of the mixture reacts with the oxygen in the air which then forms a carbamate layer or “crust” on top of the reaction mixture. This means that suitable polymerisation will not be achieved. Many reaction mixtures have this problem and they are overcome by undertaking the reaction in an inert atmosphere. This means the reactants are mixed in a glove box or glove bag, left for an induction period which can be anything between about 15 mins and one hour, depending on how reactive the components are and then the mixture is spread out on a surface to form a polymer. Obviously this is far from convenient and more often than not another route is sought, usually meaning a different, more compatible amine being sourced.

Upon mixing the glycidyl-POSS with m-XDA it was apparent that bubbles were forming within the reaction mixture. This meant that a gas was being evolved as soon as the reactants came into contact. This is not good as far as coatings are concerned

because when a film is “drawn down” or, in other words, the reaction mixture is spread out on a surface to form the polymer, if bubbles are emanating, then there are obviously many potential defect points. Sometimes this can be combated by letting the bubbles rise out of the system while in the mixing stage and by the time it comes to spread the mixture out, they have all dissipated. This was not possible in the case of the glycidyl-POSS reaction as the bubbles just kept appearing and no matter how long the mixture was left, they continued to form. Upon consultation with a colleague in the coatings industry [12] it was thought that the gas being formed was hydrogen, potentially from un-reacted H-POSS. When identifying the glycidyl-POSS by ^{1}H NMR there was no signal associated with H-POSS and it was thought that 100% conversion had been achieved. Upon further consultation with Colin Cameron it was recommended that FT-IR be used to identify any un-reacted Si-H groups. There is an Si-H absorption band at 2100 – 2360 cm^{-1} [13] and at ~2150 cm^{-1} specifically for this material. This band is associated with Si-H stretch and it appears at such a resonance that there are no other main bands, making it extremely simple to pick out and identify. In this case, when an I.R. spectrum was obtained for the glycidyl-POSS there was a sharp peak at 2150 cm^{-1} signifying that there were un-reacted Si-H groups in the starting material and that 100 % conversion had not been achieved. ^{1}H NMR had suggested that complete conversion had been achieved showing that it is not able to detect the small number of unreacted Si-H species. This meant that FT-IR would become an important tool in the successful isolation and identification of this particular compound. The original product had to be discarded and the reaction would have to be adjusted to ensure full conversion.

A procedure performed before by Liu *et al* in 2005 [3] was used which was exactly the same as that described above except that the system was heated to 100 ºC for 24 hours. When the product had been isolated in the usual manner and tested by FT-IR it was seen that there were no Si-H species present. When compared to the sample which was not subjected to reflux it was clear that 100 % conversion had been achieved. When the material was tested with m-XDA, no bubbles were formed and a clear, defect-free film was obtained. From this it can be seen that the hydrosilylation reaction requires the energy from reflux in order to proceed to completion and the target molecule had been successfully synthesised. It had also been proved that the glycidyl-POSS was compatible with m-XDA and so this system could be taken forward.

5.3.2 Synthesis and isolation of cyclic-glycidyl-siloxane

The synthesis and isolation of a cyclic comparator followed exactly the same route as the silsesquioxane derivative. There was one small change in that the procedure did not need to be undertaken under inert atmosphere conditions. The reaction was also undertaken on a larger scale since anhydrous reagents were not needed. Typically 4 g of tetrametylcyclotetrasiloxane was dissolved in 100 mL of toluene, 4 equivalents of allylglycidylether added and 200 µL of Karstedts's catalyst. The mixture was then refluxed at 100 ºC for 24 hours to ensure full conversion. The product was isolated in exactly the same way as above. FT-IR showed no Si-H signal and ^{1}H NMR showed the expected signals of the desired product and no signals associated with

tetramethylcyclotetrasiloxane. Therefore complete conversion to tetramethylglycidyl cyclotetrasiloxane had been achieved.

The product was isolated as a brown oil and was reacted with m-XDA to see if it was compatible. It reacted and a clear, defect-free film was obtained within 8 hours. This reagent could then be taken forward in the project and although it only has half the number of reactive sites as that of the silsesquioxane equivalent, could be used as a comparator in a number of systems.

5.3.3 Linear comparator

It was thought that a linear comparator should be sought to build further on the data set and diglycidylether of bisphenol-A (DGEBA) was used. This is a common reactant in the coatings industry and it was to be reacted with the same amines as the two glycidyl derivatives above as a direct comparison. Obviously there are half the number of reactive sites as the cyclic analogue but once again, this could be factored into any results achieved and would result in a complete data set of the three glycidyl molecules and any number of different amines. DGEBA is a solid at room temperature and in order to get it to react with an amine it has to be a liquid. The melting point is ~40 ºC so the sample was weighed into a sample vial and then heated up beyond the melting point using a heat gun. The amine is then added and the mixture stirred. DGEBA is very compatible with the amines used here and it meant that defect-free, clear films could be obtained.

In this chapter I will discuss the reactions and behaviour of the three glycidyl analogues when reacted with the two amines m-XDA and DODA. A number of tests were undertaken on the polymers formed and the results are discussed here also.

5.3.4 Blends of glycidyl species

Cures were set up with each of the glycidyl species with each of the amines but it was thought that blends of glycidyl-POSS and DGEBA and the cyclic-glycidyl siloxane and DGEBA should be investigated. Blends were made up as shown in Table 5.1 and all were reacted with the two amines resulting in a broad data set covering the full range of species available.

5.3.5 Testing on polymers (films)

With each specific mixture a solid polymer or film was obtained. A number of tests were undertaken on each of the polymers obtained. Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA), Thermogravimetric Analysis (TGA), Microhardness tests, corrosion tests and QUV testing, which tests the gloss retention of a coating, were undertaken.

The following set of curing reactions was set up and undertaken.

Table 5.1 Curing reactions undertaken

Epoxy	Wt. % replacement of DGEBA	Amine
Glycidyl-POSS	0	m-XDA/DODA
Glycidyl-POSS	30	m-XDA/DODA
Glycidyl-POSS	70	m-XDA/DODA
Glycidyl-POSS	100	m-XDA/DODA

Epoxy	Wt. % replacement of DGEBA	Amine
Cyclic-glycidyl siloxane	0	m-XDA/DODA
Cyclic-glycidyl siloxane	30	m-XDA/DODA
Cyclic-glycidyl siloxane	70	m-XDA/DODA
Cyclic-glycidyl siloxane	100	m-XDA/DODA

Each row in the table corresponds to two polymers and each mixture produced a solid polymer which meant that all were able to be tested and a cohesive set of results were obtained.

Thermal Stability

TGA traces were obtained to evaluate the thermal stability of the POSS-containing nanocomposites. Shown in Figure 5.3.2 are the overlaid TGA curves recorded in air at 25 ºC/min. Within the experimental temperature range all of the TGA curves display a one-step degradation mechanism with the possible exception of the 100 % POSS + DODA curve, which appears to have a slight step at about 130 ºC. This would suggest that the degradation mechanism of the standard (DGEBA + DODA) was not significantly altered by the presence of the POSS. The initial decomposition temperatures have been increased slightly by the addition of the POSS, the increase is not that significant but there is a definite increase. It can be seen that the ceramic yields increase significantly with increasing levels of POSS. Also, the rates of mass loss decrease significantly with increasing concentrations of POSS. Overall, the thermal stability of the different cures, in terms of ceramic yields and rate of decomposition was enhanced with the inclusion of the POSS cluster.

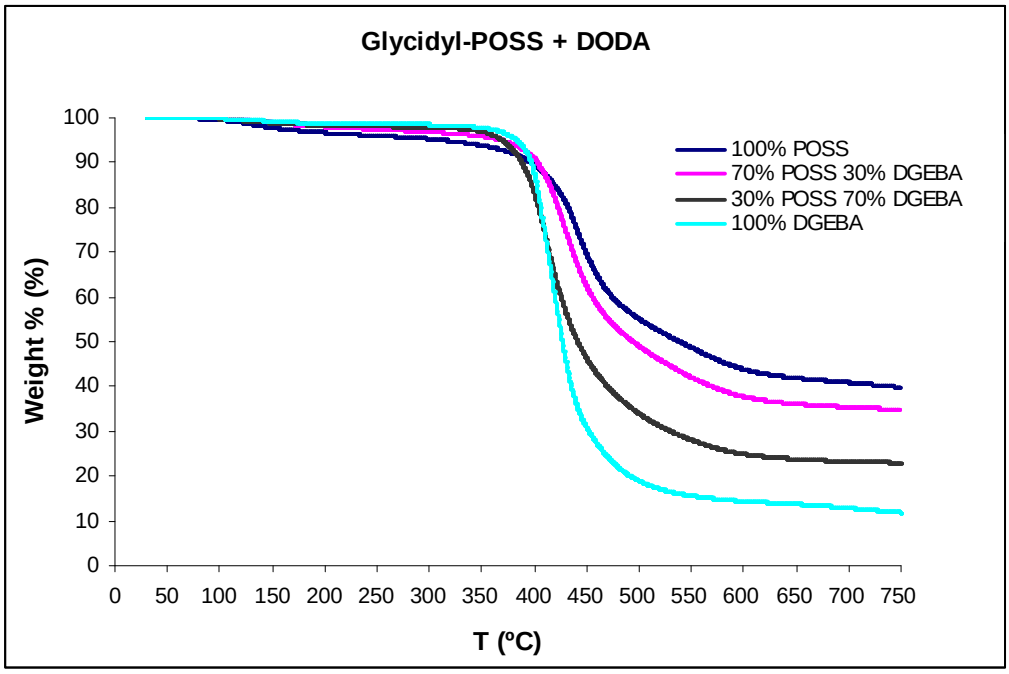


Figure 5.3.2 TGA traces obtained for glycidyl-POSS + DODA

Results for the glycidyl-POSS + m-XDA system were similar. The TGA traces are displayed in Figure 5.3.3 and it can be seen that the initial decomposition temperature of the system has increased slightly on the inclusion of the POSS cube. The ceramic yields increased significantly with the addition of POSS. There appears to be a trend with regard to the ceramic yield and the concentration of POSS. The amount of POSS present is not directly proportional to the increase in the ceramic yield. For example, the difference in ceramic yield between the 0 % POSS system and the 30 % POSS system is not the same as the difference in ceramic yield between the 70 % and the 100 % POSS systems. In other words, the rate of increase in the ceramic yields with increasing concentration of POSS decreases. This could be down to the fact that when larger amounts of inorganic material is present there is less chance that increasing the level of inorganics in the system will have an effect on

the thermal properties of the material. In other words, when there is already a significant amount of inorganic material present in the system there is less chance of observing any major changes when a comparatively small amount of extra inorganic is added to the system. The rates of mass loss are also decreased significantly with increasing levels of POSS and together with the increase in ceramic yield, show that POSS increases the overall thermal stability of these systems.

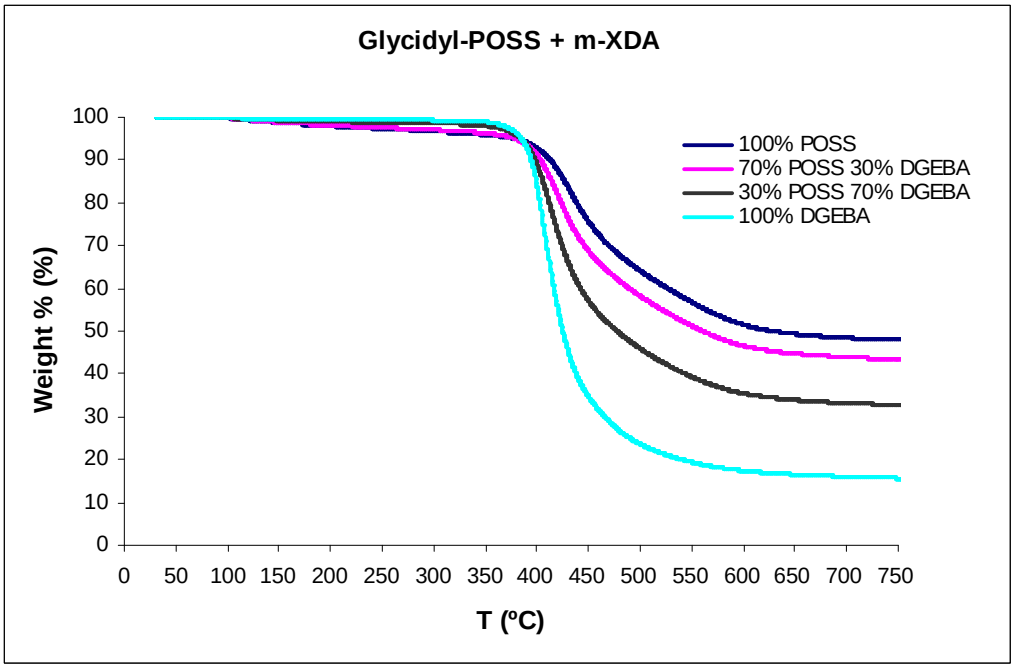


Figure 5.3.3 TGA traces obtained for glycidyl-POSS + m-XDA

The TGA results for the cyclic-glycidyl siloxane + DODA system are shown in figure 5.3.4. The traces follow a very similar pattern, suggesting the degradation mechanics are not affected by the addition of the siloxane and the initial decomposition temperatures are not significantly affected either. The ceramic yield of the system is not affected much at all, there is a slight increase in the ceramic yield as the concentration of the glycidyl species increases but the increase is very small

compared to the increase offered by the POSS cube. The siloxane ring definitely has an effect on the rate of mass loss and there is a definite relationship between the concentration of the cyclic-glycidyl siloxane and the rate of mass loss. With increasing amounts of the cyclic-glycidyl siloxane analogue present, the more thermally stable the cure in terms of rate of mass loss. There is not a huge difference between each trace but the difference between the standard and the pure cyclic-glycidyl is quite significant.

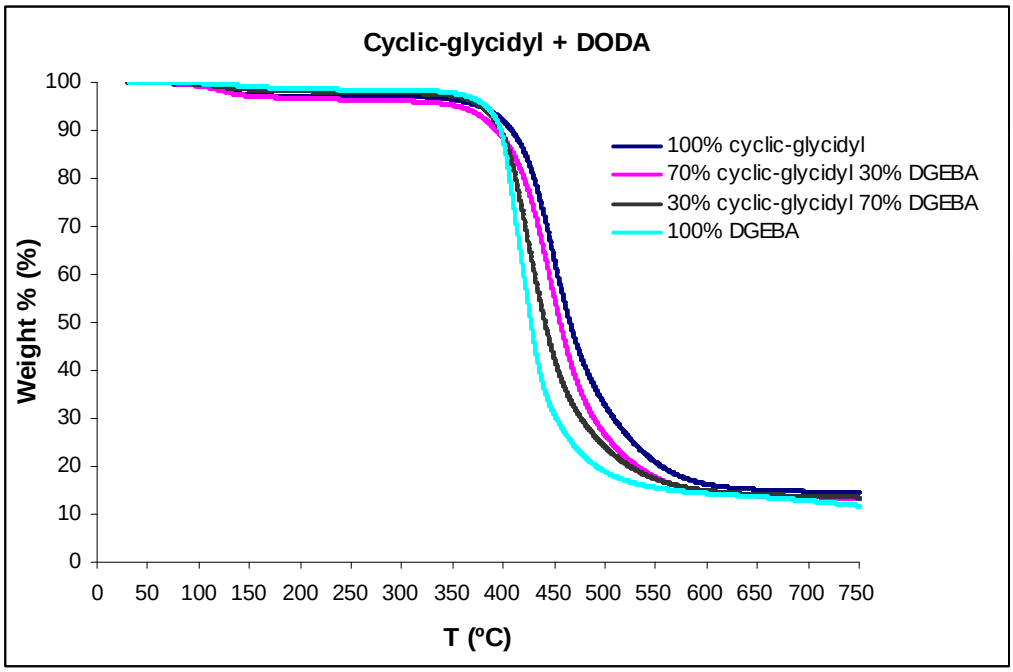


Figure 5.3.4 TGA traces obtained for cyclic-glycidyl + DODA

The TGA data obtained for the cyclic-glycidyl siloxane + m-XDA system are shown in figure 5.3.5. It can be seen that addition of the cyclic siloxane does not appear to affect the fundamental shape of the degradation. This suggests that even upon addition of this extra component, the degradation mechanics are not altered

significantly. The initial decomposition temperature does not change significantly, however there is a slight increase upon addition of the extra inorganic. It must be noted that there is no trend to this increase and perhaps the increase only occurs due to there being any sort of extra inorganic being present. The ceramic yield of the standard DGEBA + m-XDA cure is 15 %. With the addition of the cyclic siloxane there is a slight increase in this to about 21 – 23 %. There appears to be no trend to the ceramic yields obtained with the 70 % cyclic analogue 30 % DGEBA giving the highest ceramic yield. This appears to be the optimum blend to obtain the highest ceramic yield here but there is no significant change and a larger study would have to be undertaken to prove this. The rate of mass loss is affected by the amount of cyclic-glycidyl present and as the concentration increases the more thermally stable the polymer is in terms of rate of mass loss. Again there is not a large difference between the rates of mass loss of each of the blends but there is quite a significant difference between them and the standard so the addition of the cyclic-glycidyl is clearly having a positive effect on the rate of mass loss.

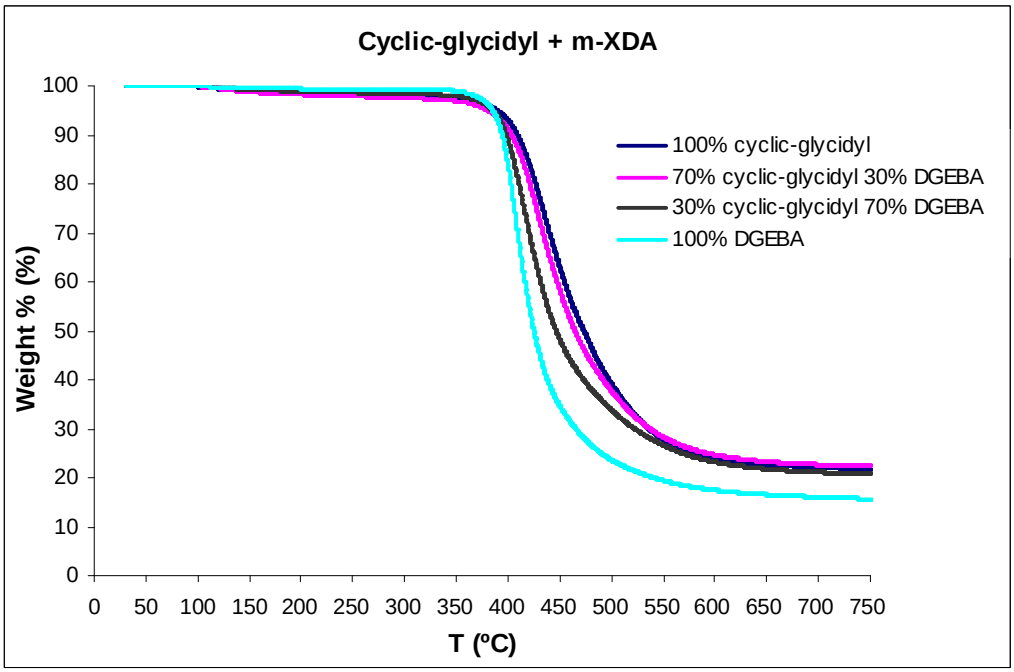
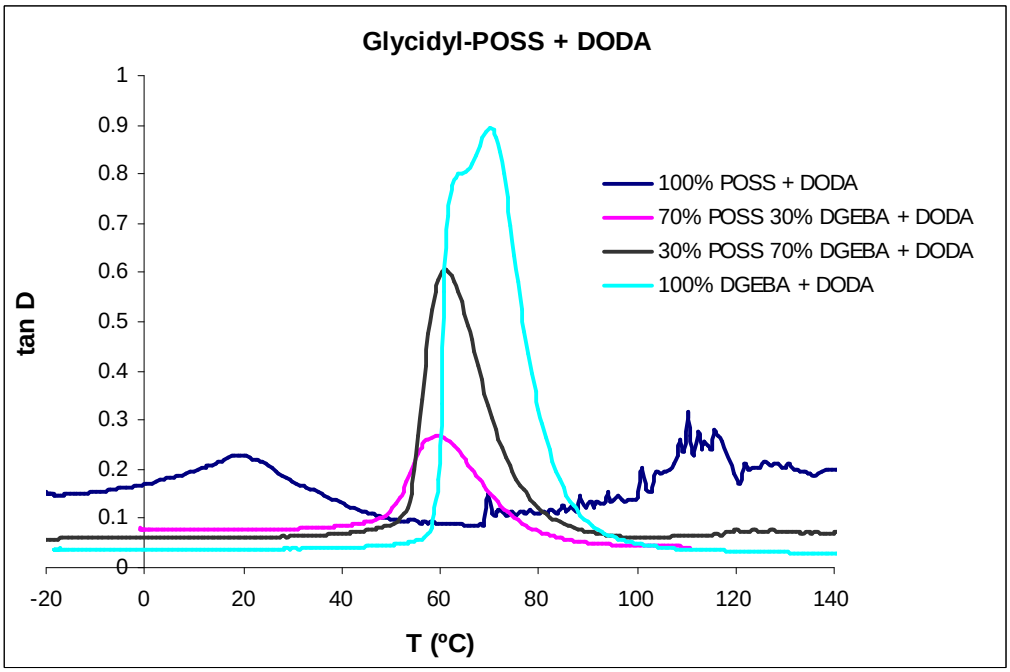


Figure 5.3.5 TGA traces obtained for cyclic-glycidyl + m-XDA

Glass Transition Behaviour

Glass transition temperatures (T_gs) were obtained for each of the POSS-containing nanocomposites by subjecting the samples to Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA). Dealing with the DMA results first, the results for the glycidyl-POSS + DODA are shown in Figure 5.3.6 where the tan δ are shown as functions of temperature. When a peak is exhibited it constitutes an α relaxation transition, which is attributed to the glass transition of the polymer. It can be seen here that the initial heats yield quite complicated spectra and making any assignments is extremely difficult. Each sample was post-cured at 120 ºC for 2 hours to see if this would simplify any of the systems. From the traces obtained it can be seen that the T_g of each system decreases as the concentration of the POSS in the

nanocomposites increases. The standard i.e. the DGEBA + DODA shows a tan δ max at 70 ºC which can be directly assigned as its T_g. The T_g for the 30 % POSS 70 % DGEBA system is 61 ºC with a well-defined tan δ and the T_g for the 70 % POSS 30 % DGEBA gives a T_g of 59 ºC. Obviously these figures are extremely close together and upon repeat runs, values of T_g were 60.1 ºC and 59.6 ºC respectively. It should be noted that the trace for the 100 % POSS + DODA is of a very poor quality. This is due to the sample slipping slightly within the clamps in the instrument which leads to a step in the tan δ curve. It looks as though the T_g was still observed and can be assigned from the tan δ max which is 19.5 ºC, significantly lower than any of the other samples. Obviously the incorporation of the POSS cube in this way is reducing the glass transition temperatures. The data obtained from the post-cured samples, also shown in Figure 5.3.6 back these statements up and clearly show that as the concentration of the POSS increases, the glass transition temperature of the system decreases.



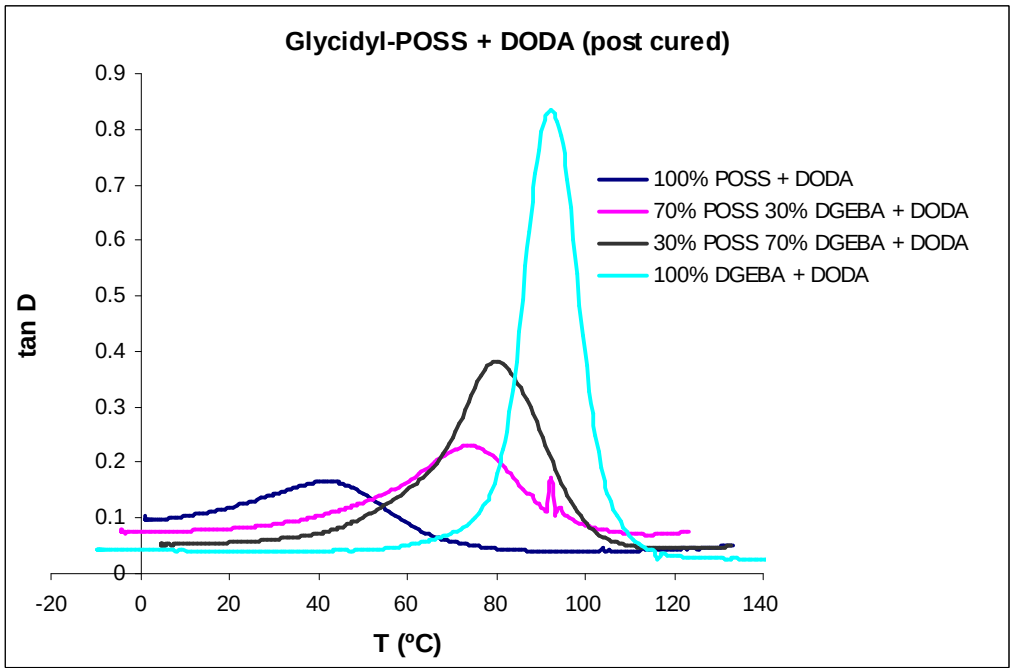


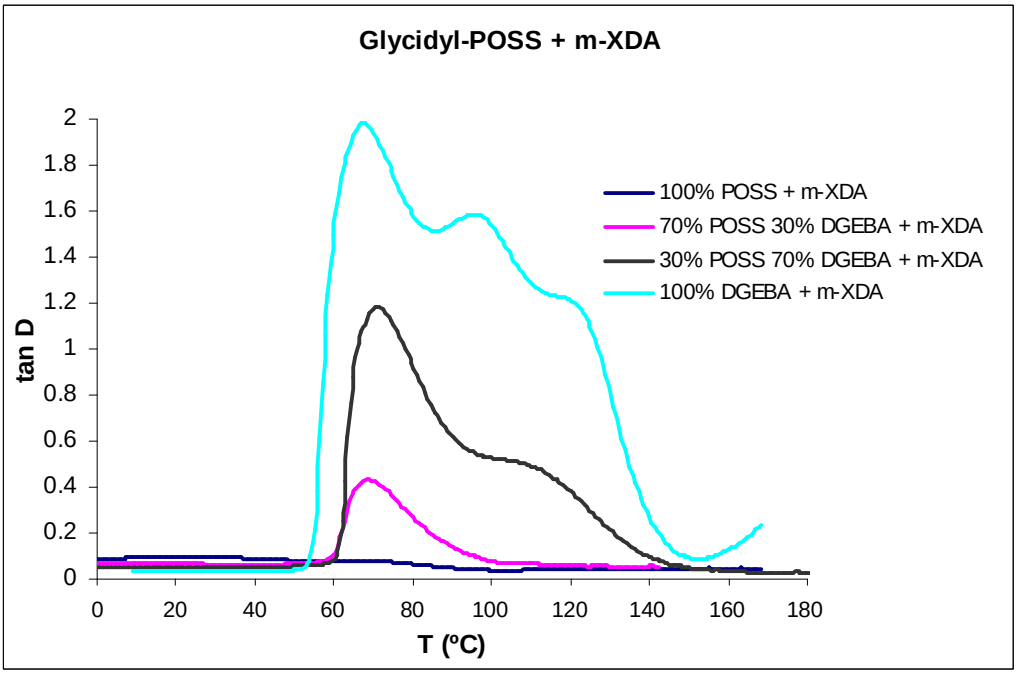
Figure 5.3.6 DMA traces obtained from glycidyl-POSS + DODA

The results for the glycidyl-POSS + m-XDA are shown in figure 5.3.7 where the tan δ are shown as functions of temperature. From the results obtained it can be seen that

this is a very complicated system and there are obviously more than one simple transition present. It is a very complex trace with two peaks and a shoulder and being able to assign any individual feature is very difficult. The same can be said of the 30 % glycidyl-POSS 70 % DGEBA system. The trace obtained is complex and assigning a definitive T_g is difficult. The trace obtained for the 70 % POSS 30 % DGEBA + m-XDA was a lot simpler to interpret and there is a definite tan δ max which gives a T_g of 68 ºC but unfortunately there is nothing to compare this with. The glycidyl-POSS + m-XDA trace yields quite a complicated tan δ plot. This shows that there are a large number of processes at work here and being able to assign each of them and discuss the result is impossible.

It should be noted that managing to get a sample for DMA was extremely difficult due to the extremely brittle nature of this nanocomposite. Every time a sample was obtained that matched the dimensions required, it shattered as it was loaded onto the instrument. In the end a sample of non-uniform size and shape was used so perhaps the results, while giving a good picture of the mechanical strength of the material, cannot be described as definitive.

The data obtained from the post-cured samples are a lot more conclusive with each trace yielding a single peak. Each peak can be directly assigned to the T_g of each system. As with the glycidyl-POSS + DODA system, the T_g of each species decreases as the concentration of the POSS increases showing that the incorporation of the extra species lowers the thermal stability of the coating in terms of glass transition temperature.



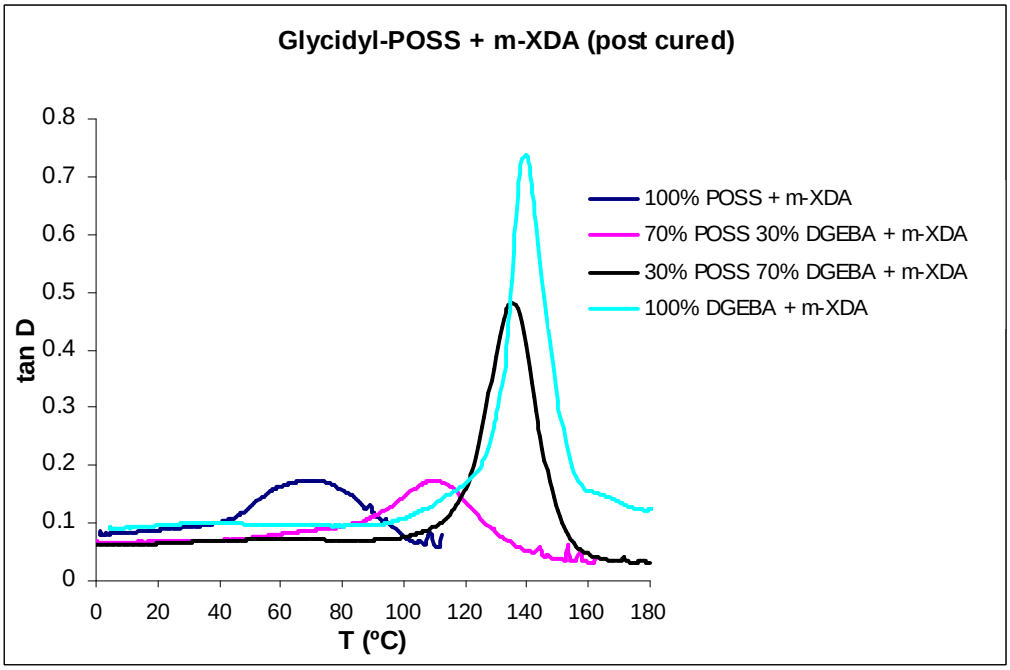
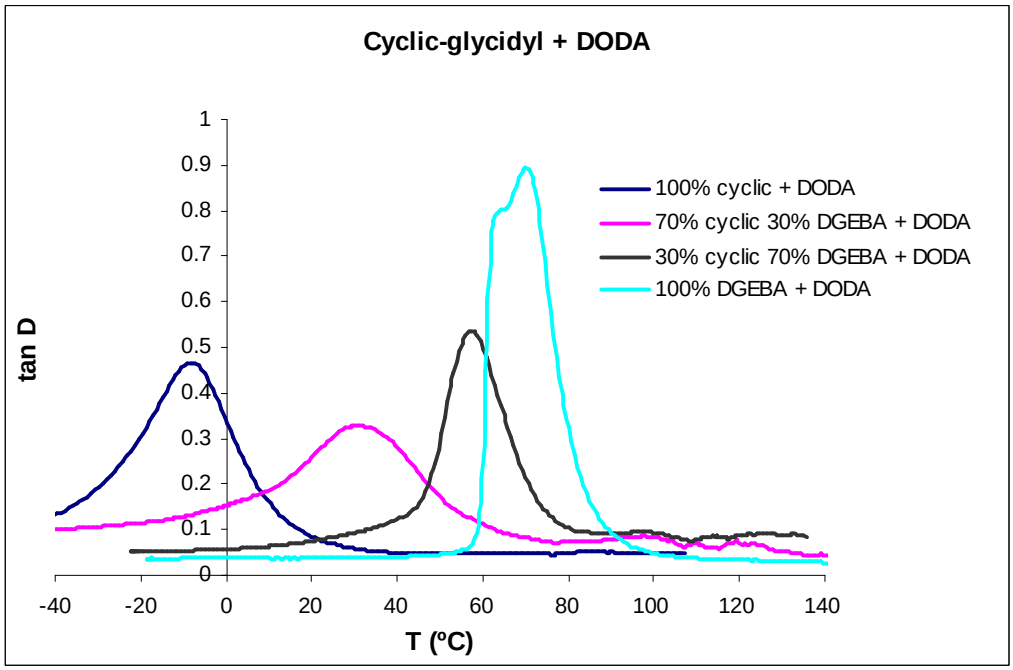


Figure 5.3.7 DMA traces obtained from glycidyl-POSS + m-XDA

The results for the cyclic-glycidyl siloxane + DODA are shown in Figure 5.3.8 where the tan δ are shown as functions of temperature. From the results obtained it is shown

that the standard proves to be the most stable in terms of glass transition temperature. As already discussed, the T_g of the system is 70 ºC. The 30 % cyclic-glycidyl siloxane 70 % DGEBA system has a T_g of 57.3 ºC. This is a significant decrease and the trend continues with the 70 % cyclic-glycidyl siloxane 30 % DGEBA + DODA system which yields a T_g of 31.3 ºC. This decrease in T_g is further compounded with the DMA trace of 100 % cyclic-glycidyl siloxane + DODA which yielded a T_g of -7.7 ºC. The trend shown here is quite conclusive in that as the concentration of cyclic-glycidyl siloxane in the cure increases, the associated T_g decreases. The post-cured samples verify this with four well defined T_g peaks which show exactly the same thing.



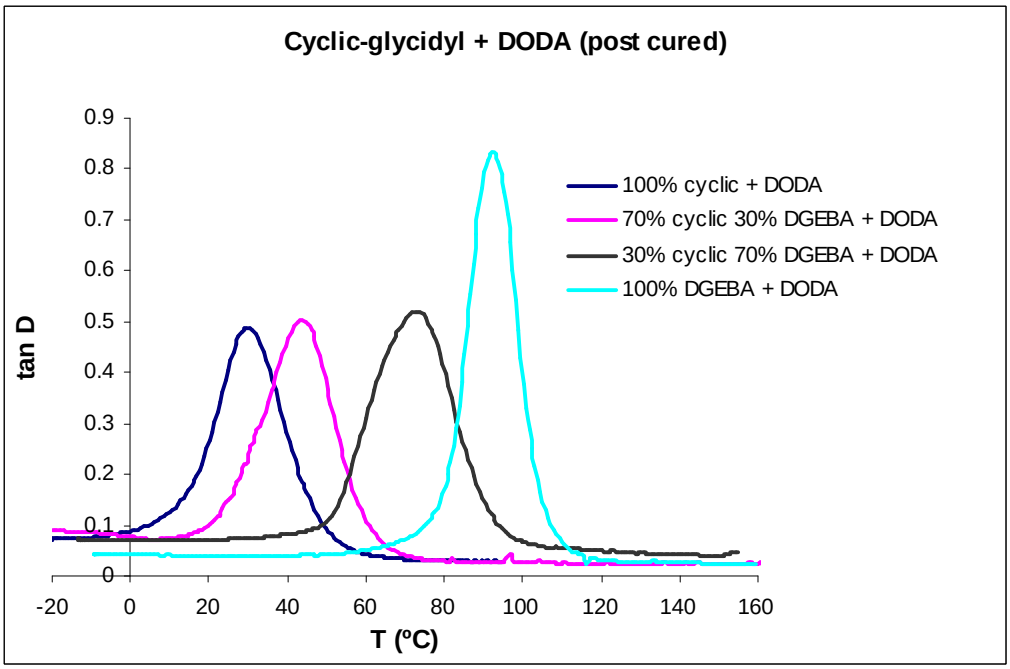
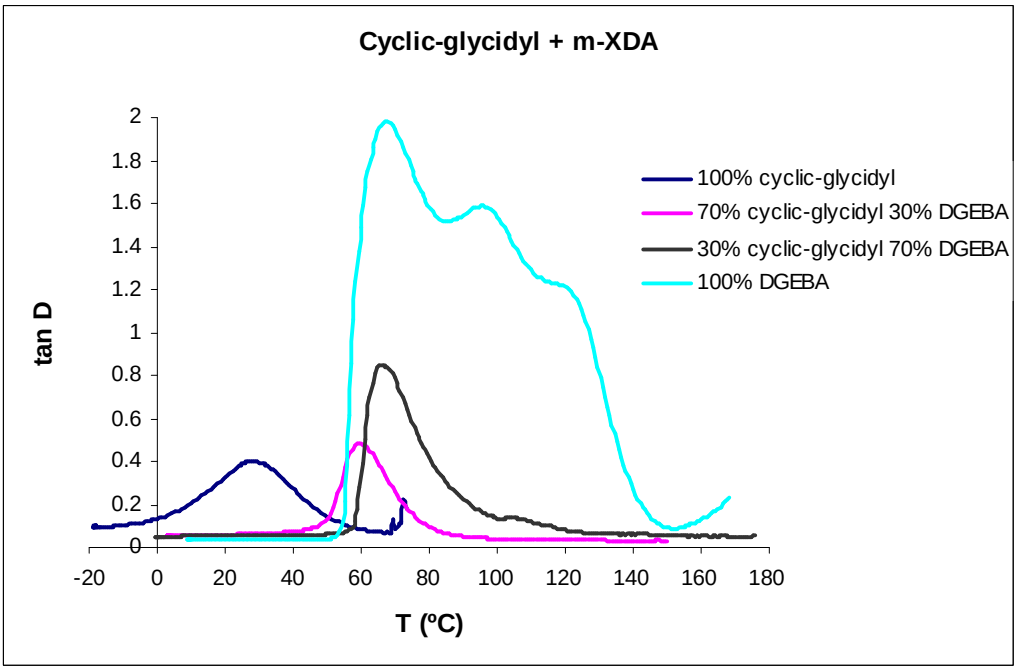


Figure 5.3.8 DMA traces obtained from cyclic-glycidyl + DODA

The results for the cyclic-glycidyl siloxane + m-XDA are shown in Figure 5.3.9 where the tan δ values are shown as functions of temperature. As already discussed, the standard yields far too complex a trace to be able to assign anything. The 30 % cyclic siloxane 70 % DGEBA cure showed a glass transition temperature of 66.2 ºC. A decrease in T_g was observed when the 70 % cyclic-glycidyl siloxane 30 % DGEBA system was investigated. A T_g of 59.7 ºC was assigned to the system as it had a simple peak. This decrease in T_gs as concentration of cyclic material increased was further realised with the DMA trace of 100 % cyclic siloxane + m-XDA which yielded a T_g of 28.4 ºC. The post-cured data are also shown in Figure 5.3.9 and confirmed the fact that as the concentration of the cyclic-glycidyl siloxane increased, the T_g of the system decreased. It should be noted that the post-cured traces for the 70 % cyclic-glycidyl siloxane 30 % DGEBA and the pure cyclic-glycidyl siloxane + m-XDA appear to be quite complicated, however it can still be seen that the trend outlined above still fits.



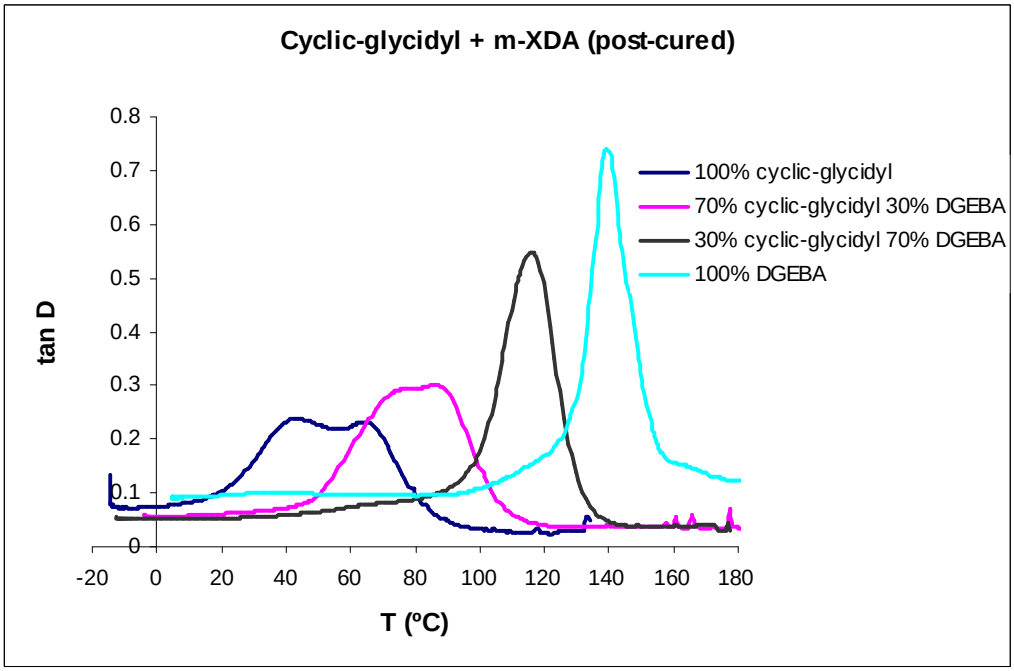


Figure 5.3.9 DMA traces obtained from cyclic-glycidyl siloxane + m-XDA

It can be seen that the post-cured samples give a much more cohesive set of results due to the α relaxation transitions being a lot more well defined. This is to be

expected as the extra energy eliminates any un-reacted species, yielding a much more homogeneous system. This leads to much less complex systems and the desired polymer is all that remains, giving good, definite glass transition temperatures.

The behaviour of the glass transition temperatures of the various systems and blends were also investigated by DSC. The results obtained are a lot more complicated than those obtained from DMA but they can be compared. A trace was obtained for each cure and are displayed and discussed below. For each system an initial heat and a re-heat were undertaken. This is standard practice and means that any un-reacted species left in the cure are driven off during the re-heat due to the extra energy. Obviously this leads to much more coherent, clear data as all of the complicated signals that are present in the initial heat have been removed and the sample is a much more homogeneous system. The glass transition temperature assignments made from here are from the re-heat as this was the only way to successfully identify the events taking place in the sample. It should be noted that by doing this, a T_g of the ambient-cured system is not yielded.

The DSC data for the glycidyl-POSS + DODA system are shown in figure 5.3.10. It can be seen that as predicted the initial heat yields a very complicated trace and not a lot can be taken from this. The initial heats obtained from the 70 % glycidyl-POSS 30 % DGEBA + DODA and the 30 % glycidyl-POSS 70 % DGEBA + DODA do yield a T_g but they are not as well defined as those yielded from the re-heat. The exotherms could also be investigated and area of the peaks could be measured to study the extent of reactions. This is extremely difficult to undertake here as the

traces are very complex and trying to obtain an accurate peak area would be extremely difficult. As can be seen from the traces, as the concentration of the POSS increases, the T_g obtained from the re-heat, decreases. The standard yields a T_g of 80.7 ºC but the rest of the traces yield quite complicated traces meaning that assigning T_gs is very difficult. The results are in good agreement with what was obtained from the DMA data and confirms that the glass transition temperatures decrease upon addition of the extra inorganic material.

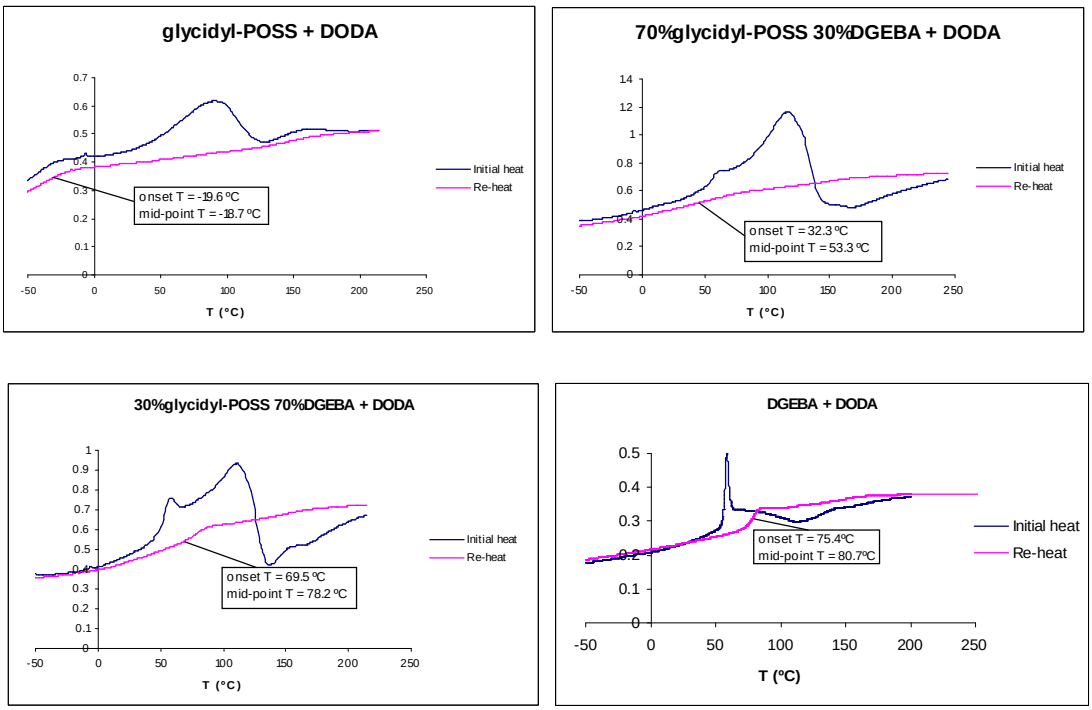


Figure 5.3.10 DSC traces obtained for glycidyl-POSS + DODA

Figure 5.3.11 shows the results obtained from the glycidyl-POSS + m-XDA system. The first runs yield T_g transitions which show an additional excess enthalpy peak due to physical ageing but again the traces are too complex to yield anything useful. The re-heats are where the most information is contained and although being able to

assign definite T_gs being difficult it can be seen that as the concentration of the POSS increases, the T_g decreases.

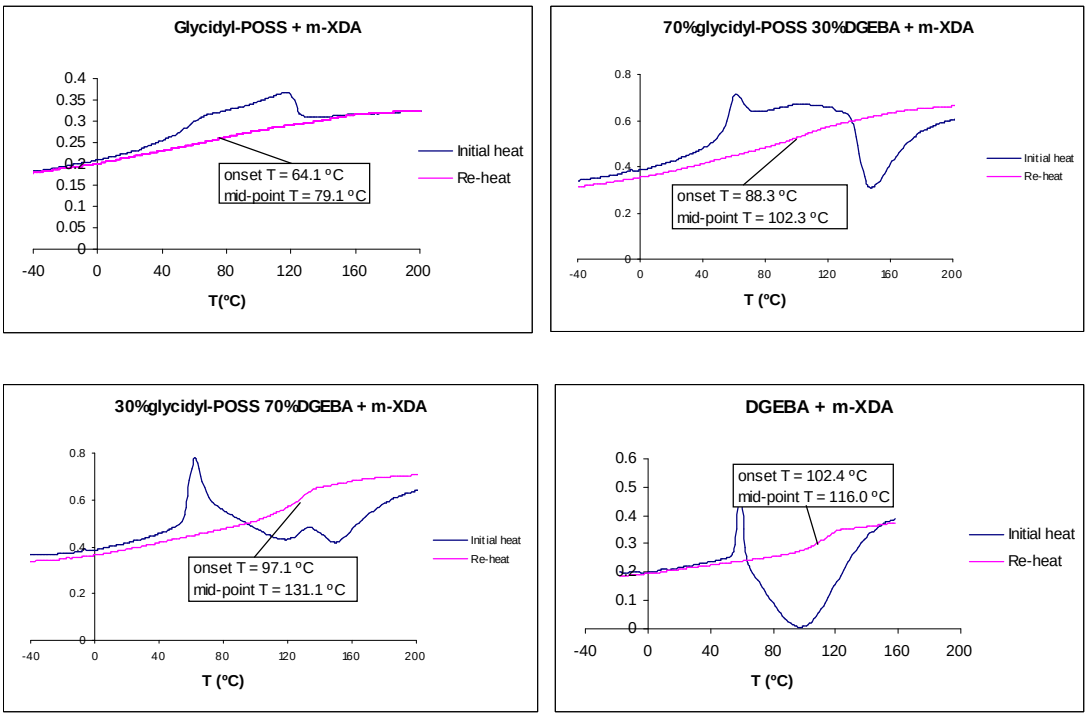


Figure 5.3.11 DSC traces obtained for glycidyl-POSS + m-XDA

The results for the cyclic-glycidyl siloxane + DODA are displayed in figure 5.3.12. As before, the initial heats are too complicated to analyse and nothing of any note can be taken from these. Again, the exotherm peaks would yield information on the extent of cure but obtaining accurate peak areas is impossible. Any information yielded comes from the re-heats and it can be seen that the pure cyclic-glycidyl siloxane + DODA gives a mid-point T_g of 17.3 ºC while the 70 % cyclic-glycidyl siloxane 30 % DGEBA + DODA shows a slight decrease in T_g with an equivalent temperature of 6.9 ºC. This was an unexpected result but the temperatures yielded are very close together so it is extremely difficult to take any firm conclusions from this.

The 30 % cyclic-glycidyl siloxane 70 % DGEBA + DODA system yields a T_g of 25.2 ºC, a significant increase which shows that as the concentration of cyclic-glycidyl siloxane decreases, the T_g increases. The standard yields a T_g of 65 ºC, another significant increase and a result which further backs up the statement above.

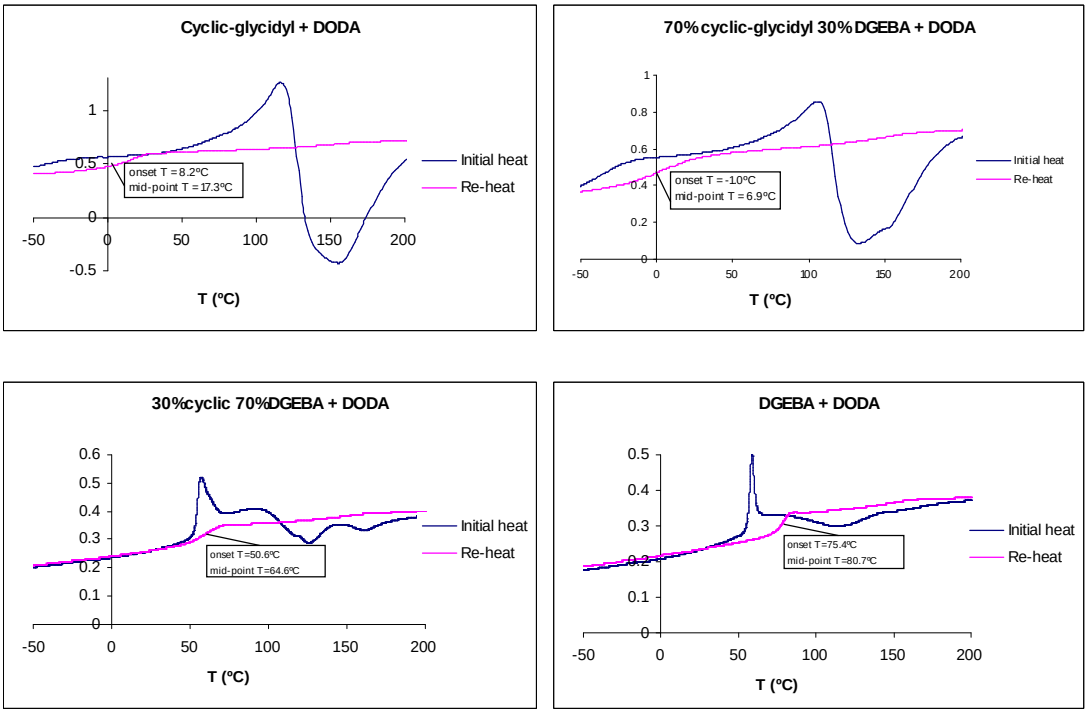


Figure 5.3.12 DSC traces obtained for cyclic-glycidyl siloxane + DODA

The cyclic-glycidyl siloxane + m-XDA DSC traces are shown in Figure 5.3.13. The initial heats do not yield much which can be analysed but the re-heats give clear glass transitions. As can be seen from the glass transition information on each trace, as the concentration of the cyclic-glycidyl siloxane increases the T_gs decrease. Again, this is in agreement with the DMA data and shows that the added cyclic-glycidyl siloxane has the effect of reducing the glass transition temperatures of the systems.

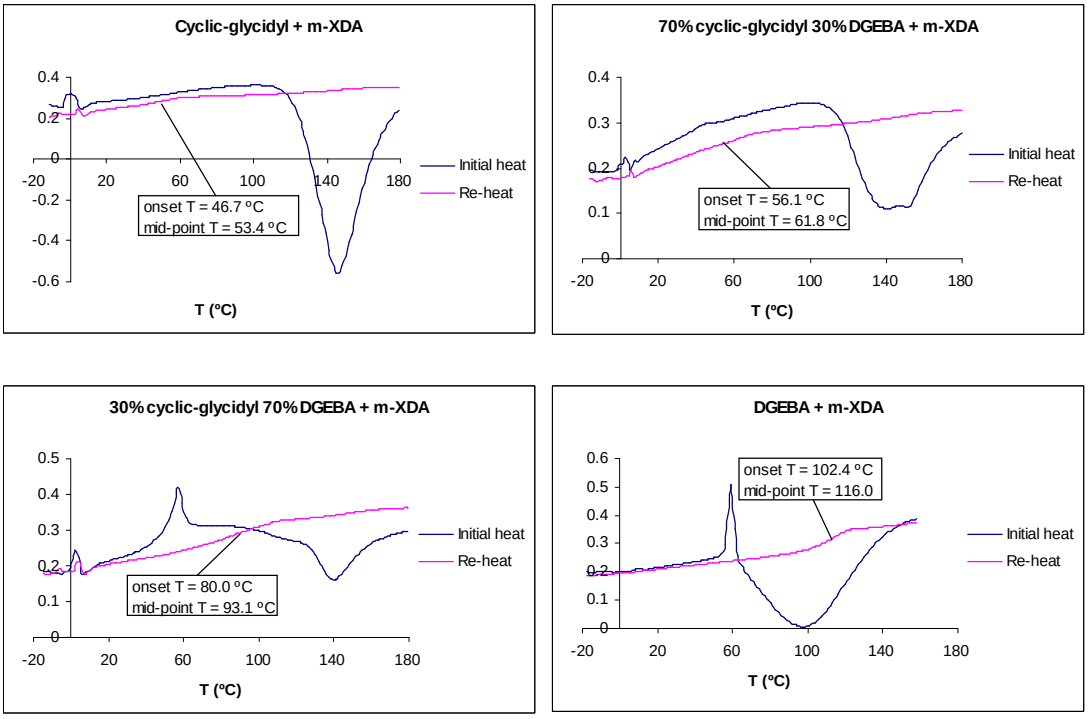


Figure 5.3.13 DSC traces obtained for cyclic-glycidyl siloxane + m-XDA

Microhardness Tests

A key measurement in the testing of polymers and coatings is the hardness of the sample. Each film discussed thus far was tested on a Fischerscope® H100C microhardness instrument. This instrument can measure hardness in the range 0.001 – 120,000 N/m^2 with a load range of 0.4 – 1000 mN and an indentation depth of 700 μm. The tests undertaken here used a Vickers diamond indenter and the coatings had to be undertaken on glass slides in order for them to be tested. The instrument measures a number of different parameters, the key ones being EIT, Elastic Modulus (GPa), W_t Total Work (nJ), W_e Elastic Work (nJ), W_r Plastic Work (nJ). The main

parameter studied here is HM Martens (Universal) Hardness, measured in N/mm^2 which is calculated from the depth of indentation at the maximum load. Martens hardness takes both elastic and plastic behaviour into account so is probably the best value to compare.

The results obtained are shown in figure 5.3.14. Each figure is a mean value which was obtained from six measurements at different points on the sample.

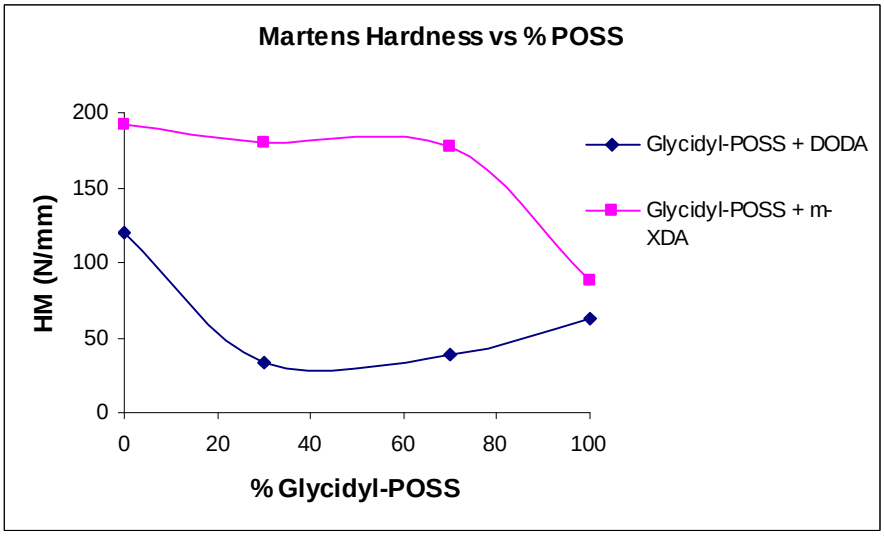


Figure 5.3.14 Hardness data obtained from glycidyl-POSS + DODA and glycidyl-POSS + m-XDA

From the results obtained from the glycidyl-POSS + DODA system it can be seen that as POSS is incorporated into the system the hardness of the coating obtained decreases significantly. After the initial decrease, there appears to be an increase in hardness as the concentration of POSS increases. The differences are extremely

small however and are probably not all that repeatable, extensive studies would have to be undertaken and that was not possible here.

The results obtained from the glycidyl-POSS + m-XDA show that as POSS is incorporated the hardness of the samples remain relatively constant. It is difficult to definitely say that the trend seen here is what would happen on repeat runs but as this was only undertaken once it is impossible to say. There is no significant decrease in performance as POSS is incorporated until the pure POSS sample which yielded a significant decrease in hardness.

Figure 5.3.15 shows the microhardness data for the cyclic-glycidyl system.

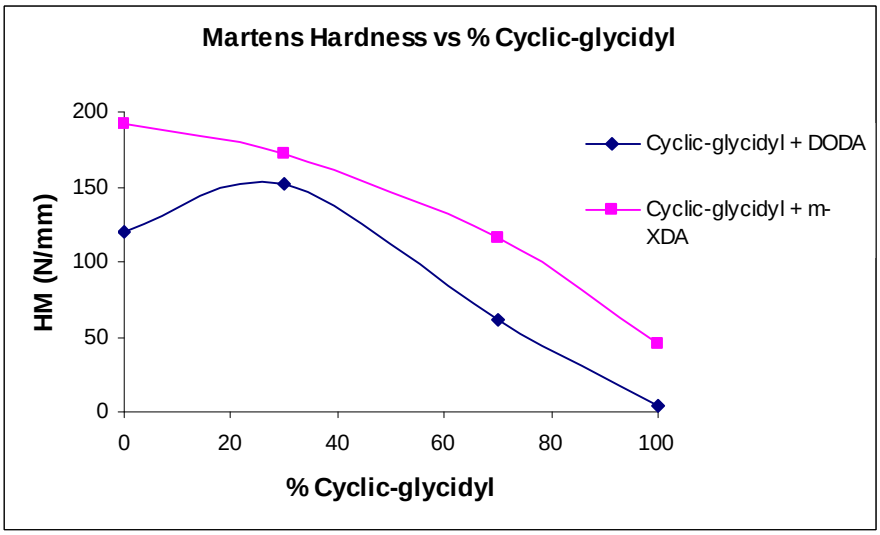


Figure 5.3.15 Hardness data obtained from cyclic-glycidyl + DODA and cyclic-glycidyl + m-XDA

The first thing that should be noted here is the poor quality of the data. Neither of these systems yielded good coatings in terms of hardness. The values yielded from the cyclic siloxane + DODA appear to show an increase in HM from the 100 % DGEBA to the 30 % cyclic-glycidyl 70 % DGEBA systems and then a decrease in hardness as the concentration of the cyclic-glycidyl increases further. It would be difficult to take any firm conclusions from this and more studies would have to be undertaken. The coatings obtained formed opaque solids with rough surfaces so finding six locations for the diamond tip to take a representative value for hardness was extremely difficult. There are definitely some compatibility issues with the cyclic material and DODA and with such poor hardness values it can be seen that this is the case.

The films obtained from the cyclic siloxane + m-XDA were, once again of a poor quality. As with the DODA system the surfaces were particularly poor with them not being clear and there being effects which can only be describes as “wrinkles”. This meant that if the instrument indenter hit one of these higher parts there would be a lower hardness result compared to if it measured a part of the coating which was quite uniform and evenly spread out on the glass. This had to be taken into account and some anomalous results which were achieved had to be investigated further to see if they should be included in the average. From the graph it can be seen that as the level of cyclic-glycidyl siloxane based material in the system increased, the hardness decreased in an almost linear fashion. Once again, these results raise questions about the compatibility of the cyclic-glycidyl siloxane and the amine and show that these cures are not all that useful in terms of coatings obtained.

Overall, it is difficult to draw any real conclusions from the microhardness data. These systems had to be tested in this way and this has been undertaken successfully but more investigation would have to be undertaken to draw any firm conclusions.

Corrosion Data

In the coatings industry new materials are tested for their corrosion qualities. This is achieved by incorporating the material into a paint, spreading the paint onto a grit-blasted steel panel, drilling a hole through the paint to reveal the steel underneath and then subjecting the panel to an automated programme of dry and salt-water conditions in a salt fog chamber. Obviously the exposed part of the steel panel will begin to corrode and depending on how the paint performs, this corrosion will spread across the panel. If the paint performs well, the panel should not be affected too much by the salt water and conversely, if the paint performs poorly the panel will be visibly affected by the corrosion.

It was thought that the corrosion qualities of the glycidyl-POSS should be investigated. This meant incorporating the material into a paint which would then cure and a solid coating would be obtained. Two different glycidyl-POSS systems were investigated, one where the POSS molecule was incorporated in a stoichiometric fashion and another where the POSS was added in a volume replacement fashion. It should be noted that the volume replacement coating had roughly twice the amount of glycidyl-POSS present as the stoichiometric coating.

Four panels were produced for each coating and the programme or cycle they were subjected to was 1 hour at ambient temperature in salt fog then 1 hour “dry” at 35 ºC. The salt solution is 0.35 % ammonium sulphate, 0.05 % sodium chloride and this was undertaken in an Ascott S450t salt fog chamber.

Shown below in figure 5.3.16 are photographs of each of the coatings after 11 weeks in the chamber. As can be seen there is significant corrosion present and the coatings did not perform particularly well but not significantly worse than the standard. This could be down to the performance of the coating or the standard of the technique used to apply the coating to the steel panel. There were definite defects present after the paint mixture had cured and although attempts were made to fill these with an inert epoxy, these had a significant effect on the performance of the paint. This is down to human error in the application method, mainly due to inexperience, and since there were only four panels of each sample produced, the chances of minimising these errors are small. Having said that, it was important to undertake these tests and although many more would have been desirable it was not possible due to problems obtaining large amount of the glycidyl-POSS.

Standard Stoichiometric Vol. Rep.

Figure 5.3.16 Corrosion data obtained for the industry standard compared two different POSS-based coatings.

It can be seen that all of the panels have been affected by the salt fog, including the standard, which shows that the problems with the application process probably outweigh the actual effect of the coating. The samples with the least amount of corrosion present were the ones with the thickest coatings and obtaining consistent sample thicknesses was a problem. It can be seen that the addition of POSS does not have a detrimental effect on the anti-corrosion qualities of the paint systems investigated.

QUV Data

Another technique used in the coatings industry which tests gloss retention in paints was used. QUV testing was undertaken and consists of subjecting a paint or coating

to UV rays over a particular time span and then measuring the gloss retention of the paint by measuring how the reflectance of the paint has been affected.

Again, two different POSS systems were investigated, one where the POSS molecule was incorporated in a stoichiometric fashion and another where the POSS was added in a volume replacement fashion. Panels are produced on aluminium sheets and subjected to 4 hours UV at 60 ºC using UVA-340 fluorescent tubes then 4 hours condensation at 45 ºC all in a Q-Panel QUV-SE weatherometer.

The results obtained are shown below in figure 5.3.17. As can be seen, the POSS-containing systems perform well up until about 2700 hours. At this point the gloss retention of the three systems begins to decrease significantly but it should be noted that the standard does not particularly outperform the two POSS-containing paints. It was important to test gloss retention and although more samples would have been desirable, it was not possible at this juncture. The results show that upon addition of POSS, the paint systems perform relatively well and it appears that incorporating POSS does not diminish the gloss retention of this particular paint system.

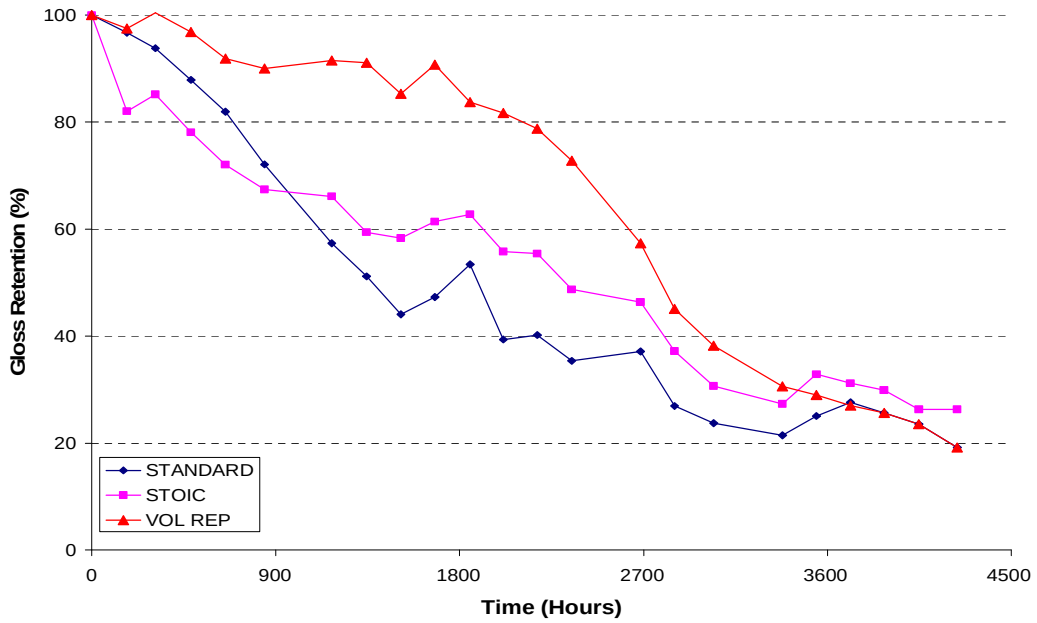


Figure 5.3.17 Gloss retention data obtained for two POSS-based paint formulations compared to an industry standard. Note that the volume replacement POSS formulation performs particularly well up to 2700 hours.

5.4 Conclusions

A series of POSS-containing systems were prepared via curing reactions with both DODA and m-XDA. A series of blends were set up and tested with POSS being incorporated with DGEBA. Each system yielded solid polymers at ambient. As a direct comparator to the POSS cluster, a cyclic siloxane was incorporated into the same series of curing reactions. Also, a series of blends were investigated with the cyclic-glycidyl incorporated with DGEBA. Each cure yielded solid polymers at ambient. All polymers produced were tested by TGA, DMA, DSC and were subjected to microhardness testing.

The TGA data show that the initial decomposition temperatures of the cures are increased slightly by the incorporation of POSS. This could be due to the addition of the extra inorganic and the stabilising effect of the POSS cube increasing the thermal stability of the polymer in terms of its initial decomposition temperature. With regards to the rate of decomposition, as the concentration of POSS increases, the rate of decomposition decreases. This shows that the addition of POSS leads to a different decomposition route and one where the rate of mass loss is significantly diminished. Again this shows that POSS is having an effect and is increasing thermal stability. The ceramic yields obtained from the POSS-containing cures are significantly higher than those where POSS is not present. This is not a major surprise as the addition of an extra ceramic will always increase the ceramic yield but the increase is a significant one. This shows that the POSS nanocomposite improves the thermal stability of this system in the ways described. This could be related to the 3-D nature of the molecule and the stability that is built up from the network that is formed.

Addition of the cyclic siloxane system led to the initial decomposition temperatures of the systems being increased slightly, the rates of decomposition being decreased and the ceramic yields increased. Obviously this has to do with the extra inorganic material being incorporated and it can be said that the systems studied here were found to be more thermally stable with regards the parameters investigated here. It would appear that this extra stability comes from the siloxane ring and it can also be seen that the ring does not have as profound an effect as the POSS cube.

The data obtained from the DMA were far from straight forward but there are certain results which can be extracted. Here we discussed the tan δ values and what can be yielded from these. What was shown was that as the concentration of the additional inorganic, be it the POSS or the cyclic siloxane, in each system increased, the glass transition temperature obtained from tan δ decreased. This is probably down to the fact that glass transition temperatures essentially measure the degrees of freedom associated with the system. Here, that is the organic "arms" that are associated with the POSS molecule. As the concentration of these organic groups increase, the less stable the polymer obtained becomes in terms of glass transition temperatures.

The DSC data were in good agreement with the DMA results. Having said that, the data produced from the DSC was a lot more complicated but the same observations were made. As the level of inorganic in the system increases there is a decrease in the glass transition temperature. This is probably due to the reasons described above and the DSC confirmed the observations made with the DMA.

The microhardness data primarily showed that the films were not very hard. Each system only had one film which could be tested in this way so the observations seen here may not be entirely representative. There were definite issues regarding compatibility with some of the amines, particularly with the cyclic-glycidyl siloxane material however a film was obtained and data was obtained for each system. Time constraints meant that further investigation was not possible but this is something which would have to be studied in more detail if there was more time available.

The corrosion and QUV data shows that upon addition of POSS, performance of paint systems were neither compromised nor improved upon. Having said that, only a very limited number of samples were investigated and had more raw materials been readily available, more experimentation in these areas would have been undertaken. What can be said is that these techniques were used as they are used in the coatings industry and it was important to show that tests had been undertaken where POSS was present.

One of the main problems with this work was being able to synthesise large amounts of the raw materials. Attempts to scale up the H-POSS synthesis were unsuccessful, it should be noted here that large companies that specialise in POSS production have not managed to scale up the H-POSS synthesis either as it is extremely expensive to buy ca. £1000 for 10 g [5]. This meant that production of glycidyl-POSS was extremely slow and producing significant volumes for extensive testing in paints, producing more films for mechanical testing and being able to produce a full range of blends with DGEBA was not possible. This is a major drawback for any potential applications of octafunctionalised POSS species. If more raw materials were readily available more prohesion panels and microhardness data would have been obtained and a more thorough study of these would have been achieved.

5.5 References

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6. Residual Materials and Near Infrared Studies

6.1 T_{10} Species

6.1.1 Introduction

As previously described, during the synthesis of hydride-POSS there are a number of residual products produced. The most common include the T_6, T_{10}, T_{12} silsesquioxane derivatives [1], see figure 6.1.1, ladder silsesquioxanes [2], see figure 6.1.2 as well as many other less well-defined species. It was proposed that a portion of these residual species should be investigated with a view to including them in curing reactions of their own. Also, up until this point the “extra” materials were being discarded and since these techniques may be used industrially it makes more economic sense to work with all of the materials produced.

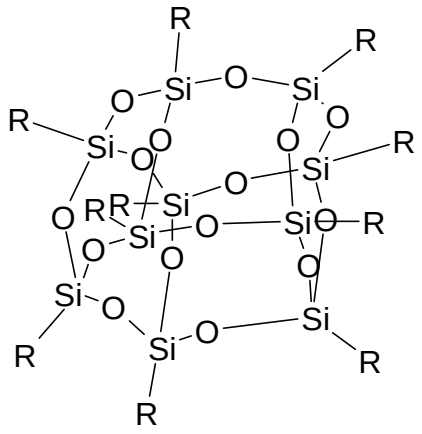

Figure 6.1.1 Schematic of the T_{10} silsesquioxane

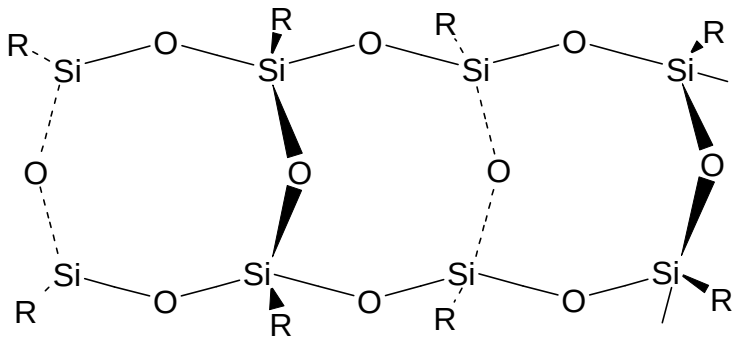

Figure 6.1.2 Example of a ladder silsesquioxane

In the process of producing H-POSS the different species are present in the reaction mixture and as the solution is reduced, the T_8 POSS begins to precipitate out [1]. The different silsesquioxane species have different solubilities which mean that they come out of solution at different times. Once the T_8 species has been collected the rest of the solution is discarded but here the remaining solvent was removed, leaving residual silsesquioxanes. It is thought that the main species present is the T_{10} hydride derivative. This is mainly down to ^{1}H NMR which shows a sharp peak at 4.10 ppm which corresponds to the T_{10} species and then a multiplet at ~ 4.12 ppm which corresponds to more general silsesquioxane compounds.

The main aim of this section of work was to see if it was possible for these residual POSS species to take place in the same reactions and with similar outcomes of the cubic

POSS compounds. It was hoped that they would be isolated and purified and then react with organic compounds in the same way as the T_8 species.

The target functionality was the glycidyl group as discussed in chapter 5. It was hoped that after the initial isolation of the residual POSS material, it would be possible to react it with allyl glycidyl ether and have it take part in the same hydrosilylation reaction as the T_8 species [3]. This would then lead to a glycidyl-functionalised POSS derivative which would take part in the same curing reactions as glycidyl-POSS and be used as a direct comparator to the cubic T_8 species. Also, these species are already present in the production of H-POSS so investigation did not involve all that much extra effort.

6.1.2 Experimental

Preparation of hydride-POSS derivatives [1]

See experimental on p 59. Once all of the T_8 H-POSS had been obtained, all of the washings were combined and reduced *in vacuo* to yield a colourless solid. (3.78 g, 7.12 mmol, 17.8% yield based on $HSiCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 4.20 (s, SiH).

Preparation of glycidyl-POSS derivative [3]

“Residual H-POSS” (0.5152 g, 0.9794 mmol.) was dissolved in anhydrous toluene (30 mL) under an argon atmosphere to which was added allyl glycidyl ether (1.4 mL, 1.347

g, 11.8 mmol.) and the solution was cooled to 0 ºC. Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst) solution in xylenes (200 μL) was added and the reaction mixture was allowed to warm to RT then placed under reflux for 24 hours until there was no Si-H absorbance visible by FT-IR. The solvent was removed to yield a colourless solid which became insoluble on isolation.

6.1.3 Results and Discussion

It was hoped that the work outlined here would add to the results achieved in chapter 5 and be used to compare and contrast directly between the octafunctional POSS and the "residual" POSS. The residual POSS material was obtained and seen to comprise mainly of the T_{10} POSS derivative by ^{1}H NMR. This consisted of a colourless powder very similar to the T_8 H-POSS. It was then thought that it should be reacted in the same way as the hydrosilylation reactions outlined in Chapter 5.

The H-POSS reaction yields "other" hydride silsesquioxanes as by-products. Once the H-POSS had been collected and filtered, the washings were combined and the solvent removed *in vacuo*. This left a colourless solid which was tested by ^{1}H NMR. When synthesising the H-POSS, there has been on occasion, in addition to the single peak at 4.18 ppm, another peak at 4.20 ppm which directly corresponds to the T_{10} species. When the residual products were tested there were a number of small peaks around 4.30 - 4.50 ppm but the predominant peak was one at 4.20 ppm, signifying the T_{10} species as the

major product with other less well-defined silsesquioxanes making up the remainder of the sample.

With these species isolated, it had to be seen if it was possible for them to take part in simple organic manipulations. It was thought that producing a glycidyl derivative was the best option and a simple hydrosilylation was undertaken. Using the method adapted from Huang *et al* [4] the residual H-POSS was dissolved in toluene and twelve equivalents of allyl glycidyl ether was added. Twelve equivalents were used so there was a 20 % excess of allyl functionality to ensure the POSS species came into close contact with the reactants in the hope of achieving full conversion. It should also be noted that there was a certain amount of conjecture regarding the number of reactive sites present. It was thought that upon consultation with Agaskar [1] and the ^{1}H NMR spectra obtained, there were on average ten Si-H reactive sites present. Therefore, it was thought that the best course of action was to use an excess of allyl glycidyl ether in an attempt to make sure the reaction proceeded.

The reaction was undertaken under reflux and after 6 hours a sample was removed from the reaction pot and the solvent was removed. A colourless solid remained and a ^{1}H NMR spectrum was sought to identify the product. Once the solvent had been removed, the product was tested for solubility in common NMR solvents. Unfortunately, the product became insoluble on isolation which meant that no NMR could be obtained. Attempts were made to use FT-IR to identify the products however these proved to be unsuccessful. Spectra had to be obtained from a mix of the product and potassium

bromide (KBr) and all spectra obtained yielded nothing. Unfortunately, therefore, it was not possible to see if the hydrosilylation reaction had taken place via the method used previously.

The reaction was halted and the solvent removed to see if the product would dissolve in any other volatile solvent. If this was possible, perhaps some curing reactions could be undertaken by dissolving the residual glycidyl material in the solvent, adding the amine curing agent, spreading the mixture out onto a suitable surface and upon evaporation of the solvent, a film might be left. Unfortunately an appropriate solvent was not found which meant that no polymerisation reactions could be undertaken.

It was concluded that at this point the work should not be continued as it appeared that the hydrosilylation reaction yielded an insoluble polymer, probably consisting of numerous glycidyl functionalized POSS materials. If this work were revisited, which would be worthwhile as another comparator to the cubic POSS species, there would have to be isolation of the different POSS species. It would be relatively simple to isolate and purify the T_{10} species as it is easily identifiable by ^{1}H NMR. Hydrosilylation of this species would stand a good chance and it was hoped that it would react in much the same way as the T_8 species. It must be stressed that there would be different isomers produced so perhaps synthesis and isolation would not be that straight forward. It is possible that any material produced will behave in much the same way as glycidyl-POSS and take part in all of the same reactions. This would mean that direct comparisons

could be made between the two and another set of data could be added to the data set achieved in chapter 5.

Being able to isolate and purify anything beyond the T_{10} species would be a lot more difficult. These species are less common and much less likely to behave in a simple manner, meaning any manipulations would be extremely difficult to undertake. Also, as shown, they are more likely to produce insoluble polymers as there are so many reactive centres present and controlling the reaction would be very difficult. Even if it were possible to obtain organic functionality on these types of species, being able to isolate, identify and characterise each one would be extremely difficult. It could be argued that in the context of this work, the formal identification of each species produced could be pointless, as long as the glycidyl functionalised species take part in polymerisation processes.

6.1.4 Conclusions

It has been shown that the residual H-POSS species have been isolated and identified to a certain extent. It was hoped that these would take part and react in a similar way to the T_8 H-POSS. Although it is entirely possible for this to happen it would be extremely difficult to identify if the reactions were taking place as any products obtained are isolated as insoluble solids.

If a glycidyl functionalised residual H-POSS species had been isolated and purified successfully it would have led to another material to take place in the curing reactions already discussed in Chapter 5. This would have meant that there was another material to add to the data set already achieved which would mean that the benefits of a non-cubic silsesquioxane could have been investigated. It is possible that the advantages which the T_8 species adds and possesses are not entirely down to the single isomer and the same benefits could be produced upon addition of any silsesquioxane species. It could lead to being able to show if the POSS cube is necessary or if the same properties can be achieved by adding a generic silsesquioxane.

Unfortunately this work was not further investigated as other areas of work were being studied but it would be interesting to return to this in the future to follow up the outstanding points.

6.2 Polybutadiene Reactions

6.2.1 Introduction

The potential use of the silsesquioxane cluster in coatings involving reactions with a polybutadiene was investigated.

Butadiene (CH_2=CH−CH=CH_2) is produced via the dehydrogenation of butene or butane and can exist in the *cis* or the *trans* form [5]. It is readily polymerised to polybutadiene (see figure 6.2.1) which is commonly used in the tyre industry, [6] and in coatings [7]. The polymerisation takes place by solution methods [5] and, depending on the composition of the polymer, there can be a variety of different properties. For example, the mechanical resilience of the polymer is significantly higher if there is a high concentration of the *cis* conformation of butadiene compared to the polymer produced from a mix of the *cis* and the *trans* conformations [5].

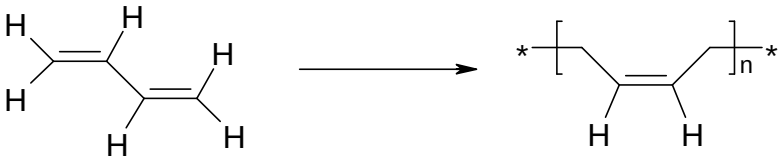

Figure 6.2.1 Polymerisation of butadiene to polybutadiene

The aim of this section of work was to investigate if hydride-POSS could take part in a hydrosilylation reaction with a polybutadiene sample. If this was shown to work then the silsesquioxane cluster would be incorporated in the matrix of the polymer and tests could be performed to see what, if anything, the POSS cluster adds to the system.

Polybutadiene is a commonly used reagent in rubbers due to its high reactivity and its numerous properties. It was proposed [8] that a sample of H-POSS be reacted with a sample of Lithene AL, which was obtained from Synthomer [9].

Lithenes are prepared by the anionic polymerisation of 1,3-butadiene using an organo-lithium initiator in a solvent which is removed at the end of reaction. This particular polybutadiene is a liquid polymer of butadiene and is used in a diverse range of applications including automotive sealants, electro-deposition paints and as adhesion promoters [5]. The Lithene “A” series of which Lithene AL is one, contain a unique vinyl cyclopentane structure. These structures are present in varying proportions, randomly distributed along the polymer backbone which together makes up the total microstructure of the Lithene [5]. There can also be a range of functionality added via chemical manipulations at ambient temperatures, something of great importance in the greater context of this work.

As previously discussed, when synthesising H-POSS there are a number of residual silsesquioxane products produced. As discussed in section 6.1 of this work, it was thought that while these species are being produced then there should be some sort of investigation into whether these additional species behave in a similar manner to the T_8 species. Also, since these "by-products" are readily available then it makes sense to investigate them.

6.2.2 Experimental

The polybutadiene sample (Lithene) was provided by Synthomer and was used as received.

6.2.2.1 Preparation of hydride-POSS [1]

See experimental on p 59.

6.2.2.2 Preparation of hydride-POSS derivative [1]

See experimental on p 132

6.2.2.3 Attempted H-POSS and Lithene hydrosilylation

H-POSS (0.2752 g, 0.648 mmol.) was dissolved in toluene (30 mL). Lithene was added (0.5416 g, 0.5416 mmol.) the mixture was stirred and the solution was cooled to 0 °C. Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst) solution in xylenes (100 μL) was added and the reaction mixture was allowed to warm to RT and stirred. Reaction mixture was tested by ^{1}H NMR and showed nothing but starting materials.

6.2.2.4 H-POSS and Lithene hydrosilylation

H-POSS (0.3270 g, 0.770 mmol.) was dissolved in toluene (15 mL). Lithene was added (0.6876 g, 0.6876 mmol.) the mixture was stirred and the solution was cooled to 0 °C. Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst) solution in xylenes (100 μL) was added and the reaction mixture was allowed to warm to RT then placed under reflux for 24 hours. The solvent was removed *in vacuo* yielding a colourless solid, insoluble upon isolation.

6.2.2.5 "Residual" H-POSS and Lithene hydrosilylation

"Residual" H-POSS (0.2666 g, 0.502 mmol.) was dissolved in toluene (20 mL). Lithene (0.5624 g, 0.5624 mmol.) was added, the mixture stirred and the solution was cooled to 0 °C. Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's

catalyst) solution in xylenes (100 μL) was added and the reaction mixture was allowed to warm to RT then placed under reflux for 24 hours. . The solvent was removed *in vacuo* yielding a colourless solid, insoluble upon isolation.

6.2.3 Results and Discussion

6.2.3.1 H-POSS and Lithene

The reaction was initially undertaken at room temperature in 30 mL of toluene and after 24 hours of stirring in the presence of Karstedt's catalyst a sample of the reaction was tested by ^{1}H NMR and it was clear that no reaction was taking place as the ratio of signal strength between the H-POSS proton and the vinyl groups was exactly the same as the ratio of the starting materials. It was thought that the reaction needed extra energy as with the previous hydrosilylation reactions (as discussed in chapter 5) therefore the system was placed under reflux. After the reaction had been under reflux for 24 hours a sample was removed and investigated by ^{1}H NMR. The spectrum obtained showed that no reaction was occurring as all that was observed were the starting materials with identical ratios of reactive centres. After consultation with industrial supervisors [8], it was concluded that there was far too much solvent present in the system, meaning that the reaction mixture was far too dilute to give an adequate rate of reaction.

The reaction was repeated with less solvent present (see section 6.2.2.4) and after 24 hours under reflux the toluene was removed *in vacuo* leaving a colourless, brittle solid.

A ^{1}H NMR was sought but the solid was not soluble in common NMR solvents. It was thought that FT-IR should be utilised as with the glycidyl-POSS hydrosilylation reaction to check whether the Si-H peak remained. A sample of the product was taken, an IR spectrum was obtained and a strong Si-H band was present, showing that there was unreacted H-POSS present and full conversion had not been achieved. The conformational make-up of Lithene means that once a POSS cube has reacted with a vinyl group in the Lithene, it is difficult for a neighbouring proton on the POSS cube to be able to come into close enough contact with another double bond in order for it to react due to sterics. This means that achieving 100 % conversion is highly unlikely. Having said that, the polymer can be investigated in the same ways as described in Chapter 5 and the appropriate conclusions can be made.

It was hoped that these reactions would take place at ambient but as discussed it was clear that no hydrosilylation was taking place and the reactions had to be placed under reflux. This is far from ideal in the context of this project as any target materials from this system would have to be heated in order for them to cure and form a solid polymer. This means that whenever a coating is sought by this method it would have to be cured at elevated temperatures which in turn yield a series of practical problems dependant on what the coating is to be used for. The reactions were undertaken nonetheless to investigate this particular material regardless of any practical problems which may arise.

6.2.3.2 “Residual” H-POSS and Lithene

The hydrosilylation reaction of the residual H-POSS and the Lithene was attempted using the same method as described above and after 24 hours under reflux in the presence of Karstedt’s catalyst, a sample of the reaction mixture was removed and the toluene was removed *in vacuo* yielding a colourless solid. Unfortunately, upon isolation the solid was not soluble in common NMR solvents so FT-IR was utilized to indicate whether full hydrolsilylation had taken place. As with the T_8 derivative, there was a large Si-H peak present indicating that full conversion had not taken place. Again this may not be all that surprising given the conformational make up of the Lithene and when paired with the relatively unknown properties of the residual H-POSS there is possibly less chance of reaction than with the often more predictable cubic POSS.

Obviously solution state NMR was not available to investigate the products of these hydrosilylation reactions but it was hoped magic angle solid state NMR could be used to signify what, if anything had occurred.

A sample from the T_8 H-POSS + Lithene reaction was investigated by ^{29}Si solid state NMR and two peaks were observed. It was thought that one corresponds to the unreacted Si from the H-POSS and one to the reacted silicon. Obviously this had to be tested and when a sample of H-POSS was observed by ^{29}Si solid state NMR a single peak was observed at -84.3 ppm which corresponds to the unreacted H-POSS. The experiment undertaken was a direct polarization (DP) which means that direct

comparisons can be made between intensities of signals. It was noted that the two peaks observed after the reaction were of extremely similar intensities and upon further study they were seen to be of roughly equal intensities. This meant that roughly half of the available protons reacted with the polybutadiene and half did not. This could be down to sterics. When one proton on the H-POSS reacts with a double carbon - carbon bond in the Lithene sample, the neighbouring protons remain unreacted as they cannot come into close enough contact with a double bond in order to react. This would mean that every POSS molecule would have the capacity to react four times. Obviously this may not be the case with each POSS cube as what is being observed is an average. It could be the case that a particular POSS cube is only reacting once or twice while another H-POSS unit is reacting with up to six or seven different carbon - carbon double bonds.

The same solid state NMR experiments were undertaken with the residual H-POSS material + Lithene sample. Obviously the starting material does not have a simple ^{29}Si NMR spectrum and there is a broad multiplet at -84 ppm corresponding to the different Si environments present. This is in stark contrast with H-POSS which obviously has one Si environment which makes assigning any transformations a lot simpler. When the residual H-POSS material + Lithene product was investigated by ^{29}Si solid state NMR there was an additional peak present at -64 ppm which shows the reacted Si environments and there was a large, broad peak at -84 ppm corresponding to the unreacted protons. Unfortunately, at this stage, it could not be seen which environments had and had not reacted. If the different Si environments had different chemical shifts and thus distinguishable peaks it may have been possible to see exactly which

environments were reacting. It is probably the case that protons from each of the different silsesquioxane species are reacting but due to the spectra obtained it is impossible to identify which ones.

6.2.4 Conclusions

Two solid polymers have been successfully synthesised from the Lithene sample and the different hydride silsesquioxane derivatives showing that they can take part in polymerisation reactions with polybutadienes. Unfortunately, these reactions did not take place at ambient temperatures which can lead to problems if the system was to be investigated more closely in applications of this sort.

The products were not able to be characterised by solution state NMR experiments here, but very early results from solid state NMR experiments produced some interesting results. It appeared that when the T_8 H-POSS was reacted with the Lithene sample, around half of the available reactive sites took part in the hydrosilylation reaction and half did not. As discussed, this may be down to steric issues with the Lithene sample only being able to come into close enough contact with around half of the protons in the sample. The solid state NMR data yielded from the “residual” H-POSS + Lithene experiment did not yield as much information due to the number of different Si environments present. It could be seen, however that the intended reaction had taken place.

If it was possible to revisit this work it would be an idea to try and purify the “residual” H-POSS material and to isolate the different species. If this was achieved, it would then be possible to investigate how each species behaves in the system.

6.3 Near-I.R. Studies

6.3.1 Introduction

Near I.R. spectroscopy utilizes the region of the electromagnetic spectrum from 4000cm^{-1} to 5000cm^{-1}. There is a very distinguishable C-O stretch found at ~4520 cm^{-1} [10] which is directly related to epoxide functionality. Since a lot of the work undertaken so far in this project has dealt with epoxides and epoxy behaviour it was thought that near I.R. spectroscopy could be a useful tool in observing and investigating any polymerisation reactions.

Having this one, well-resolved absorbance band in the spectrum means that it is possible to observe any changes in the intensity of the signal. This leads to the possibility of following the progress of a polymerisation by reacting the epoxide with an amine, collecting near I.R. data at specified times and watching as the epoxy signal diminishes. This can yield information on the extent of reaction at a given time, the gel time of the reaction or the time it takes for a solid polymer to form.

As glass does not absorb in the near I.R. region it is possible to use glass cells in these experiments. A simple glass cell was built from microscope slides and once the reactants were mixed a small amount was transferred into the cell. The cell was then taped to the I.R. spectrometer in such a way that the beam passed straight through the reaction mixture and at specified time intervals, spectra were obtained. Over time it could be seen that the epoxy signal was decreasing, showing that the reaction was proceeding.

Here, two different reactions were investigated using near I.R. namely, glycidyl-POSS + N-methyl benzylamine and glycidyl-POSS + benzylamine. Each reaction was undertaken in a glass cell and spectra were obtained at set time intervals and the results are discussed below. In this chapter each reaction will be discussed in more detail and any results obtained will be described.

6.3.2 Glycidyl-POSS + N-methyl benzylamine

6.3.2.1 Introduction

It was thought that the first reaction to be investigated by near I.R. should include an amine and one which would not lead to a cross linked polymer. With this in mind, N-methyl benzylamine was reacted with the glycidyl-POSS (see figure 6.3.1) and the results are discussed below. The reaction was undertaken in an instrument equipped with software which could collect spectra automatically at pre-defined time intervals. This meant that the reaction could be set up and left in the spectrometer for as long a period

of time as desired although most of the polymerisations dealt with here should not take longer than about 18 hours to run to completion. Spectra can be obtained every 2 minutes which leads to a large amount of data being obtained but obviously not all of the data needs to be manipulated and a lot of it can be discarded while still having more than enough to produce a coherent data set which will produce good results.

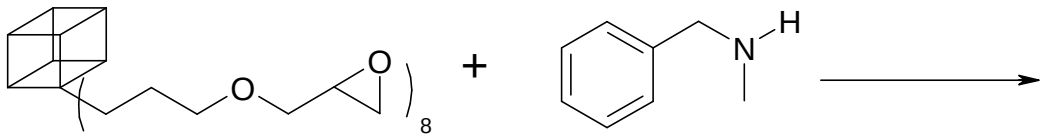

Figure 6.3.1 Glycidyl-POSS + N-methyl benzylamine

6.3.2.2 Experimental

Glycidyl-POSS (1.6679 g, 1.24 mmol.) and N-methyl benzylamine (1.2219 g, 10.1 mmol.) were mixed together in a sample vial for approx. 5 mins and transferred via Pasteur pipette to the near I.R. cell.

6.3.2.3 Results and Discussion

The reaction was set up in a sample vial, mixed and transferred to the glass near I.R. cell using a Pasteur pipette. The cell was then taped to the spectrometer in such a way that the I.R. beam passed straight through the reaction mixture. It should be noted at this

point that a background spectrum had already been obtained. Immediately after the cell had been secured in place a spectrum was obtained to yield a set of data at time = 0 or as close as possible to this. Then after a set time a spectrum was obtained and it could be seen that the peak associated with the epoxy group had diminished slightly and that the reaction was occurring. The reaction was left in the spectrometer for approximately 17 hours and spectra were obtained every 5 minutes. The results are shown below in figure 6.3.2.

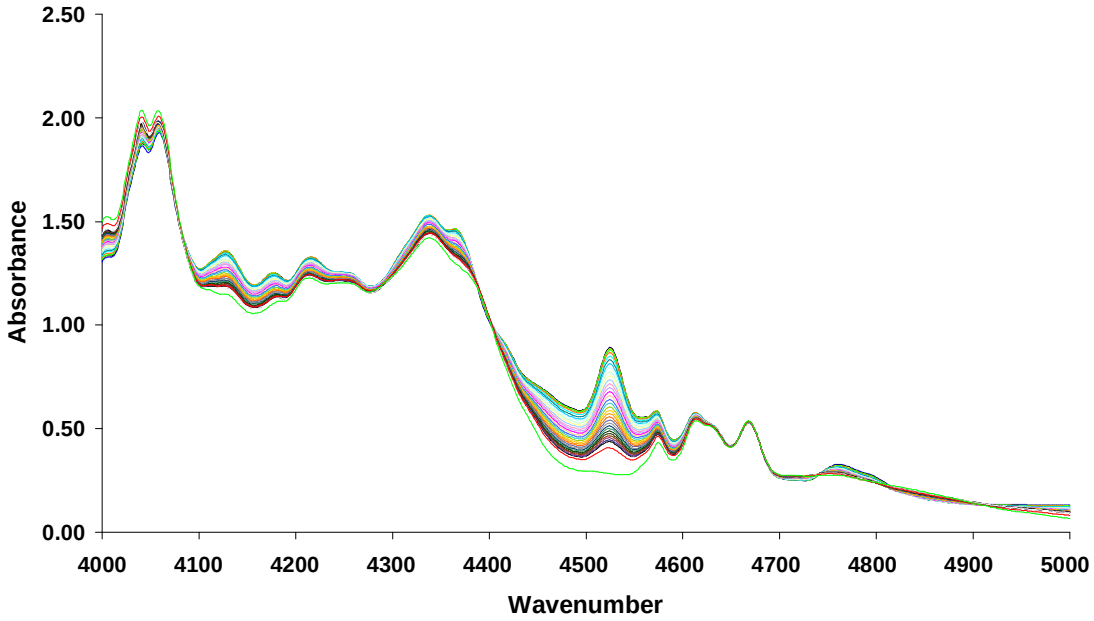

Figure 6.3.2 Near-I.R. Spectrum of Glycidyl-POSS + N-methyl benzylamine. As the reaction proceeds the intensity of the peak at 4520 cm^{-1} reduces. At the end of the experiment the polymer was heated to 100°C overnight and the IR spectrum recollected (green trace), showing no residual epoxide band.

It can be seen that the intensity of the epoxy signal at 4520 cm^{-1} reduces as the reaction progresses. The reaction was left overnight after which time it could be seen that there was a significant concentration of the amine remaining in the system. To be able to glean any information from the experiment, the reaction has to run to completion. Therefore, the cell was placed in an oven at about 100 °C to drive the reaction to completion. The cell was then placed back in the I.R. spectrometer and a final spectrum collected as shown by the green line in the figure above. It could be seen that the signal associated with the C - O epoxy stretch had gone, signifying completion of the reaction.

As this reaction was undertaken with a secondary amine, no cross-linking could occur therefore the system should be simple to study.

A graph of conversion against time is shown below in figure 6.3.3. Conversion was calculated as the difference in epoxy signal strength, after time t divided by the overall difference in the epoxy signal strength from t = 0 to full conversion. As can be seen the conversion line follows a straight line for the reaction until about t = 50, 000 when the rate of conversion appears to slow. This is expected, as the number of available reactive sites diminishes, rate of conversion will decrease as the polymer is formed. When the polymer is formed, a certain percentage of unreacted species will remain in the system but since the reaction was placed in an oven to ensure full conversion this was not observed. In fact it can be seen that when the reaction was placed in the oven and data was measured again there was a sudden step in the conversion plot to 100 %.

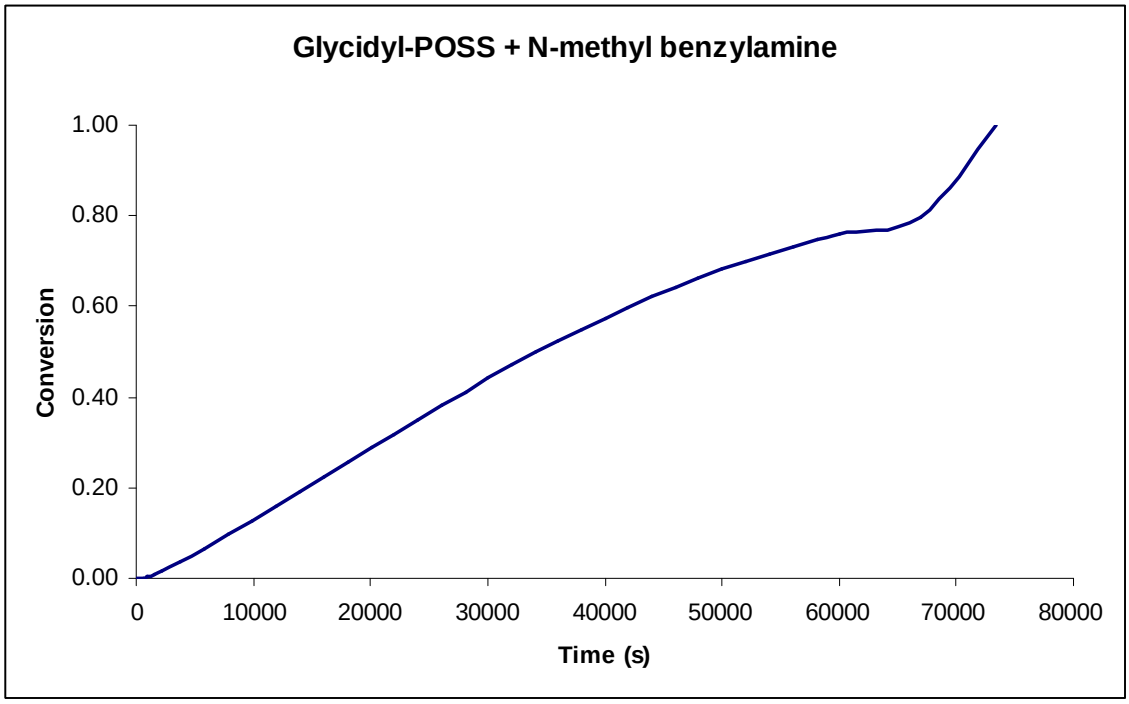

Figure 6.3.3 Plot of conversion against time for glycidyl-POSS + N-methyl benzylamine. Note that after 65000 seconds the polymer was heated in an oven, which accounts for the apparent increase in conversion.

From the conversion data, it can be seen that the rate of conversion slowed significantly after around t = 50, 000 which corresponds to a conversion figure of 0.68. Also, at around 76 % conversion the rate of reaction really flattens and no more conversion takes place at ambient. This means that around three quarters of the available reactants need to react in order for maximum ambient polymerisation to take place. It is not altogether surprising that there is a maximum in conversion at ambient because at a certain level of cross linking the motion of the monomers is necessarily impeded, meaning that the rate

of curing continues to slow. The reaction then becomes inhibited, where no more conversion can take place at ambient.

In terms of reaction kinetics, some preliminary studies were undertaken [11]. There are three parts to the reaction, the initiation, self catalysis as hydroxyl groups formed from the opening of the epoxy ring catalyse the reaction and inhibition where no more conversion can take place. It can be seen here that the maximum conversion is 0.76.

Manipulation of the curve in Figure 6.3.3 yielded figures of $k_1 = 2.44 \times 10^{-6}$ and $k_2 = 7.68 \times 10^{-6}$ where k_1 and k_2 are the two rate constants associated with the reaction [10]. One might expect k_2 to be larger than k_1 due to the self catalysis but as can be seen, these figures are extremely similar and any calculations taken from the results above could yield different results.

6.3.2.4 Conclusions

It has been shown that the glycidyl-POSS + N-methyl benzylamine system can be studied via near-I.R. spectrometry and that the results obtained yield important information about the polymerisation reaction. For example, the reaction progresses at a fairly steady rate until around 68 % conversion when the reaction began to slow significantly until 76 % conversion when the reaction appeared to stop altogether.

6.3.3 Glycidyl-POSS + benzylamine

6.3.3.1 Introduction

It was thought that the next logical step was to react the glycidyl-POSS with benzylamine (see Figure 6.3.4) and investigate the progress of reaction by near I.R. Both reagents were readily available so this seemed a suitable way to proceed. The reaction was undertaken in a glass cell in exactly the same way as the previous examples. As in the previous two examples, the spectrometer came equipped with software which could collect spectra at set time intervals so the reaction was left to proceed overnight.

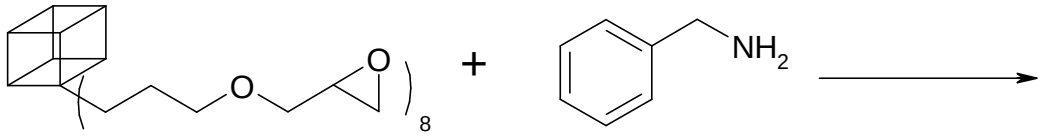

Figure 6.3.4 Glycidyl-POSS + benzylamine

6.3.3.2 Experimental

Glycidyl-POSS (1.6615 g, 1.24 mmol.) and benzylamine (0.5369 g, 5.01 mmol.) were mixed together in a sample vial for approx. 5 mins and transferred via Pasteur pipette to the near I.R. cell.

6.3.3.3 Results and Discussion

The results obtained are shown below in Figure 6.3.5 and it can be seen that the reaction proceeded as planned. There may have been a slight issue regarding the length of time the reaction was observed. It can be seen that it appears as though the reaction was still progressing when it was removed from the spectrometer. This was combated by obtaining spectra a further 24 hours after the data collection experiment. As can be seen there was still a significant epoxy signal present in the system however the reaction was investigated nonetheless.

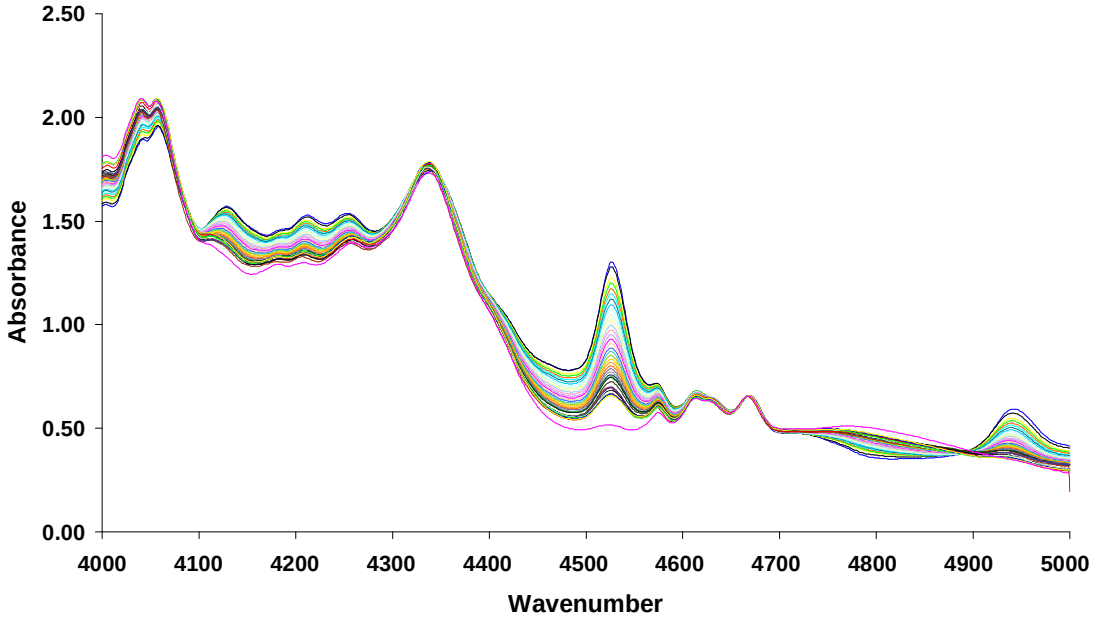

Figure 6.3.5 Spectra obtained for glycidyl-POSS + benzylamine

A graph of conversion against time is shown below in Figure 6.3.6. Conversion was calculated as the difference in epoxy signal strength, after time t divided by the overall difference in the epoxy signal strength from t = 0 to full conversion. As full conversion was never achieved, a value of absorbance which corresponded to 100 % conversion had to be obtained. This meant estimating a value of absorbance which would correspond to full epoxy conversion.

As can be seen the conversion plot follows a fairly straight line until about t = 32, 000 when the rate of conversion begins to decrease. Again, this is expected, as the number of available reactive sites decreases there is obviously a decrease in the rate of reaction. When the polymer forms, a certain percentage of unreacted species will remain in the system and it can be seen that in this example, full conversion was not achieved.

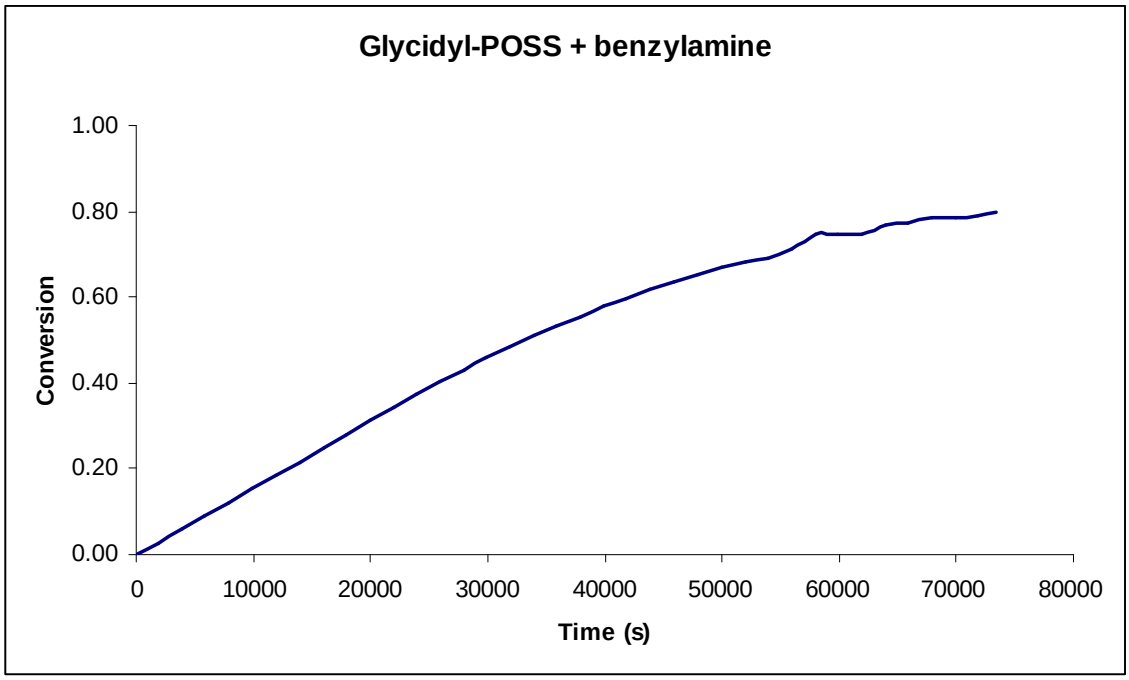

Figure 6.3.6 Plot of conversion against time for glycidyl-POSS + benzylamine

From the conversion data, it can be seen that the rate of conversion slowed significantly after around t = 32, 000 which corresponds to a conversion figure of 0.48. Also, at around 80 % conversion the reaction virtually stops and no more conversion takes place at ambient. This means that 80 % of the available reactants need to react in order for this particular polymerisation to take place.

In terms of reaction kinetics, some preliminary studies were undertaken. Again, there are three parts to the reaction, the initiation, self catalysis as hydroxyl groups formed from the opening of the epoxy ring catalyse the reaction and inhibition where no more conversion can take place. It can be seen here that the maximum conversion is 0.80

which compares to 0.76 from the previous example. This time things are a little more complicated as there is a primary amine present which is forming a secondary amine and a tertiary amine.

Using curve fitting from the data in Figure 6.3.6, figures of k_1 = 5.52 x 10^{-6} and k_2 = 4.80 x 10^{-6} where k_1 and k_2 were obtained [10]. This time, k_2 is larger than k_1 due to the self catalysis but as can be seen, these figures are extremely similar and any calculations taken from the results above could produce different rates of reaction.

6.3.3.4 Conclusions

It has been shown that the glycidyl-POSS + benzylamine system can be studied via near-I.R. spectrometry and that the results obtained yield important information about the polymerisation reaction. It has been shown that conversion follows a straight line until about 48 % conversion at which point the reaction begins to slow and eventually ceases at around 80 %.

6.4 References

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7. Conclusions and Further Work

7.1 Conclusions

The design, preparation and isolation of the appropriate silsesquioxane molecules has been a qualified success. These molecules have also taken place in the desired polymerisation reactions at ambient temperatures and the products of these have been successfully tested using methods commonly used in the coatings industry. The original aim for the industrial sponsor of this work was to see whether such ambient cure polymerisation reactions were possible. As shown in this project, this has been a success.

However, it can be difficult to obtain POSS compounds in good to high yields due to the complicated nature of the silsesquioxane cluster and the need to use extremely high-yielding reactions when attaching organic groups. Despite this, four different epoxy-functionalised POSS molecules have been synthesised, all of which show prospects for use in curing chemistry.

Perhaps the most useful epoxy-functionalised POSS compound was the glycidyl-POSS molecule [1] which was obtained and successfully synthesised in a repeatable manner with good yields which successfully participated in ambient cure reactions as discussed in Chapter 5.

The other POSS derivatives produced may have the ability to be used in the same manner as the glycidyl-POSS but the direction of the project meant that these compounds were not studied to the same extent.

The polymerisation processes at work in the curing reactions were studied. This work showed that the compounds being studied could take part in the appropriate reactions and yielded important information on controlling the stoichiometry of the polymerisation reactions. This work also went on to show that the POSS core could be incorporated into ambient-cure techniques whilst maintaining the integrity of the silsesquioxane cluster.

It must be noted that throughout the course of this work the greatest challenge has been in the preparation of the silsesquioxane starting materials. Numerous attempts were made to scale-up the octahydridesilsesquioxane (H-POSS) synthesis with no real success. It was hoped that this reaction would be undertaken in a 5 L reactor so that the H-POSS syntheses undertaken could be scaled up by a factor of two and that large amounts of H-POSS would be produced on a regular basis but corresponding yields were never obtained. The relatively slow production of the starting material meant that producing large amounts of the glycidyl-POSS was very difficult and very labour intensive. This is a major disappointment as to develop these particular routes to multifunctional POSS materials a good, industrial/commercial route would be a great advantage. Unfortunately, the lack of success in scaling up this synthesis severely

limited the characterisation techniques that could be used to fully understand the polymerisation reactions of these very interesting materials. It is very telling that since the beginning of this project we have become aware of similar efforts by a commercial POSS manufacturer (Hybrid Plastics) to develop cheap and efficient routes to this molecule, but they have also been limited in their success. Clearly the best result that can be hoped for in this area is that a completely new route to H-POSS is discovered.

As discussed, any polymers yielded from the glycidyl-POSS were to be tested via traditional coatings tests which often require large quantities of products. For example, tensile tests can be undertaken on films using an instrument which requires quite a large sample of the film (~ 5 cm x 1 cm). The sample is then placed between two clamps and the clamps are slowly moved apart and a measurement of the force used to break the sample is taken. To undertake this experiment, five samples are required which come from a coating which can use up to 10 g of the starting material. This meant that this test could not be undertaken as it was not possible to produce the appropriate quantities of glycidyl-POSS at the same time as producing enough material for the other tests.

With a POSS system in place there were a number of other areas of work investigated. In the production of H-POSS [2] there are a number of other species produced and it was thought that these should be investigated. As already described in Chapter 6 the main side-product which is present in the reaction mixture is the T_{10} hydride silsesquioxane. Much less is known about this species but it appeared to behave in a similar way to the T_8 species with respect to the hydrosilylation reaction with allyl glycidyl ether.

Unfortunately, it was impossible to confirm if a glycidyl derivative had been synthesised because the products consisted of insoluble solids. This was probably down to the fact that there are many different forms of the silsesquioxane present and whenever the reaction was undertaken, it leads to a network of products. This of course meant that isolation and characterisation of products was impossible. If this work was re-visited the T_{10} species would have to be isolated before any further manipulations were undertaken. Even if this strategy was followed there would be no guarantee of the work being a success due to the number of different isomers of the species.

The reactions between H-POSS and the polybutadiene were a success in that the reactions took place and solid films were produced. Unfortunately the reactions did not take place at ambient temperatures which was the aim however there were studies undertaken on the polymers by solid state NMR. It was not possible for these solids to be tested in the same way as described in Chapter 5 as other avenues of work were being investigated.

The Near I.R work was a partial success with two different systems investigated. The major goal of this work was to identify the extent to which the polymerisation reactions had occurred. In all cases it was obvious from residual epoxide bands in the IR that the maximum conversions only reached ~80% at ambient, although at 100 °C the reaction could be speeded up to approach 100% conversion. In principle, near IR could be used to gain even more kinetic information. Unfortunately, this is very dependent on the

relative positions of the bands in the spectra and was not possible in the systems studied here. This work could have been expanded upon by investigating any number of different systems but time constraints meant that this was not possible.

Another of the major aims of the project as a whole was to see if incorporation of POSS into a polymer through more than one linkage could induce similar increases in material performance as has been claimed for certain polymers where the POSS molecules has been introduced as a pendant group. In general the thermal and mechanical analysis undertaken in this project has not shown overwhelming evidence for significant improvements of this kind. However, one result that was extremely promising was the QUV studies where standard gloss retention experiments indicated that the POSS polymers tested performed extremely well compared to the industry standards (Figure 5.3.17 p.125). This work shows enough promise to mean that POSS-based polymer coatings could have a role to play. However, as stated above, the major limitation for industrial use is the problem in scaling up synthesis so that manufacture can be commercially possible.

7.2 Further Work

It has been shown that POSS systems can be incorporated into ambient-cure techniques but there is a lot of progress to be made.

As already discussed in the conclusions section the synthesis of sufficient amounts of starting materials proved to be one of the largest challenges faced. Perhaps more investigation is required into the H-POSS synthesis or perhaps some studies could be made into using the vinyl-POSS [3] or another POSS molecule as a precursor.

A range of epoxy-functionalised POSS molecules could be investigated and compared. This would yield information on whether varying the constituent make-up of the organic groups on the POSS has any effect on the properties of any polymers obtained. All of this information could be added to the data set outlined in Chapter 5 of this work.

A key area to investigate would be the investigation of adding a generic silsesquioxane to the systems to see if the POSS cluster is actually required. In other words, does the almost symmetric nature of the POSS cube add anything or could this be replicated by adding say, a linear silsesquioxane. Again, any polymers obtained from these systems could be directly compared to the data achieved in Chapter 5. The glycidyl functionality appeared to be the most promising in this project so this could definitely be taken forward. The length of the carbon chain could be varied to study the effects of the length

and size of the glycidyl substituent which could be directly compared to the data already achieved.

Another material which could be studied in more detail is the T_{10} glycidyl analogue. When this was studied originally the materials investigated were a mixture of the residual products. If this were to be revisited there would have to be a purification step added so that one species was being observed. This would probably be the T_{10} species to begin with and then if this proved to be a success then other silsesquioxane analogues could be investigated. Once again, any results obtained from this could be added to the data set achieved in Chapter 5 as direct comparisons could be made.

The polybutadiene reactions could be studied in a lot more detail. The problem with the species investigated in this work was that they were far too complex. The reaction could be revisited but with the different silsesquioxane derivatives isolated. This way, studying the products would be a lot simpler. This could then lead to a completely new set of ambient cure reactions to study using the numerous tests as already used in this project. If this were possible the organic manipulations required to produce suitably functionalised POSS molecules would be greatly reduced but as already discussed the problems associated with the H-POSS synthesis may pose to be too great. The properties gained from the addition of the polybutadiene [4, 5] may add completely new and interesting properties to any coatings prepared.

The near I.R. work is something which should be investigated further. The work which was undertaken in this Ph.D was at a very early stage and there is a lot of potential for this. Numerous different reactions could be investigated involving the different systems, both realised and proposed. This could lead to the polymerisation reactions being studied in a lot more detail and a better understanding of them being achieved.

Introducing different functionality to the POSS systems is something which should be investigated. Instead of epoxy functionalisation, thiiranes could be investigated. Thiiranes can be synthesised directly from epoxides [6, 7, 8] and demonstrate similar reactive qualities. It would be hoped that these molecules could be prepared and reacted with different curing agents with similar success to the epoxy compounds already discussed. If this were the case, then any polymers produced could be directly compared to the data set already achieved. These types of compounds, if produced, could then be incorporated into all of the proposed reactions as discussed above to compare and contrast with the epoxy POSS compounds.

7.3 References

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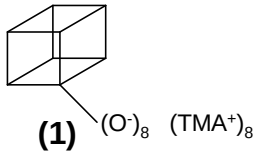
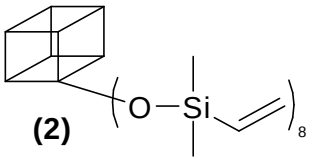
8. Appendix

8.1 Molecular Structures

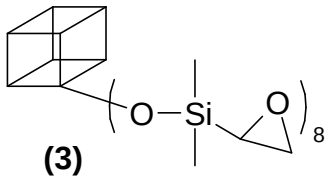
All POSS cores (Si_8O_{12}) are drawn as cubes for clarity. Only one organic "arm" is shown also.



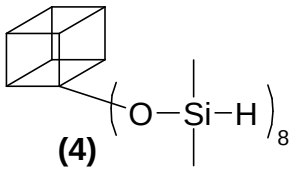
Tetramethylammonium silicate



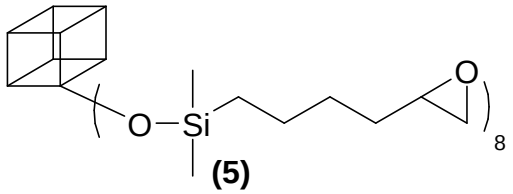
Octakis(vinyldimethylsiloxyl) octasilsesquioxane



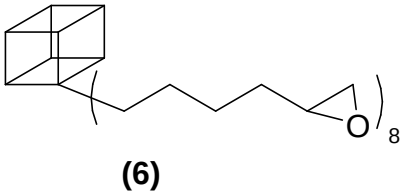
Octakis(epoxydimethylsiloxyl) octasilsesquioxane



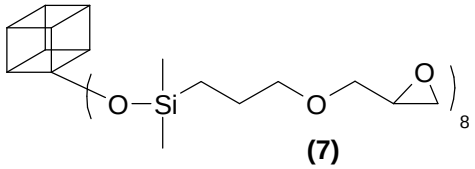
Octakis(dimethylsiloxyl) octasilsesquioxane



Octakis(dimethylepoxyhexanesiloxyl) octasilsesquioxane

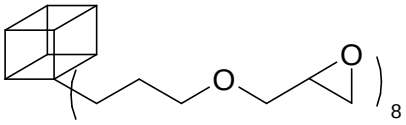


Octakis(epoxyhexane) octasilsesquioxane



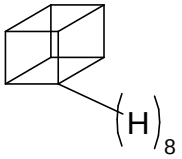
(7)

Octakis(dimethylglycidylsiloxyl) octasilsesquioxane

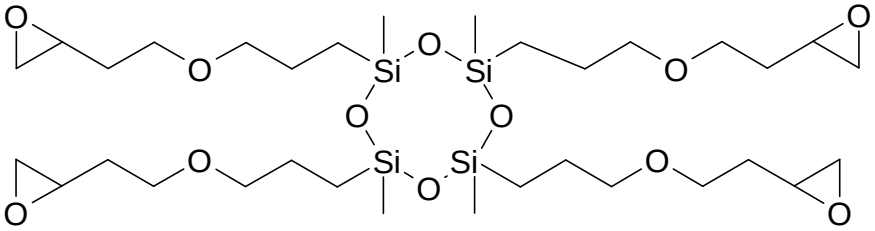


(8)

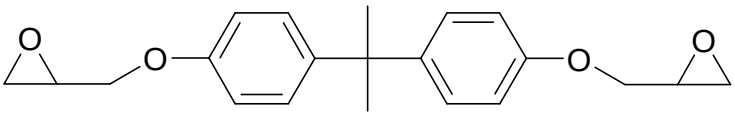
Octakis(glycidyl) octasilsesquioxane



Octahydridesilsesquioxane (Hydride POSS / H-POSS)



Tetramethylglycidyl cyclotetrasiloxane



Di-glycidyl ether of Bisphenol A (DGEBA)