This is to certify that the

thesis entitled

EFFECT OF PHENYL-FUNCTIONAL STRUCTURED SILANOL
ON THE NETWORK FORMATION OF
EPOXY-AMINE SYSTEMS

presented by

Madhu Namani

has been accepted towards fulfillment
of the requirements for

Master's degree in Chemical Engineering

Major professor

Date January 27, 2003

EFFECT OF PHENYL–FUNCTIONAL STRUCTURED SILANOL ON THE NETWORK FORMATION OF EPOXY-AMINE SYSTEMS

By

Madhu Namani

A THESIS
Submitted to
Michigan State University
In partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE
in
CHEMICAL ENGINEERING

Department of Chemical Engineering and Materials Science

2003

ABSTRACT

EFFECT OF PHENYL–FUNCTIONAL STRUCTURED SILANOL ON THE NETWORK FORMATION OF EPOXY-AMINE SYSTEMS

By

Madhu Namani

The type of R- group on trisilanol polyhedral oligomeric silsesquioxane (POSS) ($R_7Si_7O_9(OH)_3$) can affect the acidity of the –OH group present. Trisilanol phenyl POSS was found to be more acidic since the phenyl group on the silicon atom increased the acidity of the silanol group[1]. Based on the fact that acidic alcohol systems like phenol accelerate the epoxy amine curing reaction, the effect of trisilanol phenyl POSS on the curing kinetics of the epoxy amine reaction was studied on commercially available epoxy resins like diglycidyl ether of bisphenolA, DGEBA and tetraglycidyl diamino diphenyl methane, TGDDM with diamine terminated polypropylene oxide, Jeffamine D-230 and 2, methyl 1,5 pentadiamine, DytecA as curing agents. We observed a significant increase in the glass transition temperatures T_g for TGDDM amine systems containing trisilanol phenyl POSS under low temperature curing conditions. Dynamic Mechanical Analysis (DMA) was performed on cured epoxy amine samples containing trisilanol phenyl POSS, varying from 0 to 1.0% and the glass transition temperature was determined from the $\tan\delta$ peak. Fourier Transform Infrared Spectroscopy (FTIR) experiments was used to study the curing kinetics in epoxy amine systems with and without trisilanol phenyl POSS. It was observed that the trisilanol phenyl POSS initially improves the rate of the secondary amine reaction with the epoxy leading to increased consumption of amine and epoxy, thereby forming a network having higher glass transition temperatures.

dedicated to my parents……….

ACKNOWLEDGEMENTS

I would like to express my sincerest thanks to my advisor, Professor Andre Lee for his support, guidance, and leadership throughout my graduate education. In addition I would like to thank Professor Krishnamurthy Jayaraman and Professor Michael Mackay for serving on my Master's Defense Committee.

I would like to thank Dr. Bruce Fu who helped me with my thesis work by giving valuable suggestions and also assisted me in performing the Fourier Transform Infrared Spectroscopy experiments.

I would like to thank Dr. Haddad of Air Force Research Laboratory, for providing me with the NMR results of DytecA/ trisilanol phenyl POSS and Jeffamine D-230/ trisilanol phenyl POSS systems.

I would like to thank Dow Chemical for providing samples of DER332 (DGEBA), Huntsman Chemicals for Jeffamine D230 and DuPont Chemicals for providing samples of DytecA.

Last, but not the least, I deeply thank my parents and family for their emotional and financial support and their never-ending encouragement throughout my education.

TABLE OF CONTENTS

CHAPTER 4

CHAPTER 5

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

Epoxy resins are the most commonly used engineering thermosets, in part due to their excellent engineering performance upon curing and ease of processing prior to curing. The broad interest in epoxy resins originates from the extremely wide variety of chemical reactions and materials that can be used for the curing and the many different properties that result. Depending on the chemical structure of the curing agent and the curing conditions, it is possible to obtain mechanical properties ranging from extreme flexibility to high strength and hardness and high chemical resistance which can be used to make thermosets having high adhesive strength, good heat resistance and high electrical resistance. Knowledge of the chemistry involved permits the user to cure over a wide range of temperatures and to control the network structure that can lead to the desired performance of the thermoset.

A significant amount of work has been reported in the literature concerning the nature of reaction between epoxides and amines[2]. O'Neal and Cole concluded that the only significant reaction between an epoxy resin and an amine is that of the amino hydrogens[3]. The reaction of epoxy compounds with amines is strongly influenced by the nucleophilicity of the amine. A rapid increase in the rate of amine and epoxide consumption can be induced by the catalytic effect of the hydroxyl groups generated[4]. The accelerating efficiency of the alcohol can be approximately proportional to its acidity, which explains the high catalytic activity of phenol[5]. This is because acids or electrophilic species accelerates the addition of most nucleophiles considerably by the reversible formation of the more reactive conjugated acid of the epoxide, as in the case of

Lewis acid like BF_3[6-8]. In addition to acceleration of amine- epoxides reactions via in-situ-formed hydroxyl groups, the addition of compounds containing hydroxyl groups, such as phenol, hydroxy alkylated polyamines, and adducts of oxirane or 1,2-epoxypropane with polyamines, was reported to produce greater reactivity than that of the parent amine[9]. A particular problem exists with the use of phenol as an accelerator, because it is highly corrosive to skin, co-carcinogenic[10], neurologically active[11] and is coming under increasing regulatory pressure.

The development of additional cluster-based systems amenable to a broad range of materials application has been of considerable intrest given the continuing demand for new or retrofitted materials with enhanced properties. One class of compounds potentially suited for such development is polyhedral oligomeric silsesquioxanes (POSS). A surge of recent activity in this field has been directed primarily towards the application of POSS compounds in catalysis[12].

Silsesquioxanes play an important role in the development of heterogeneous silica supported transition metal supported catalyst systems. Octameric silsesquioxane resemble skeletal frameworks found in crystalline forms of silica and zeolites, and their rigid framework makes silsesquioxanes suitable models for silica surfaces. Of particular intrest are the incompletely condensed silsesquioxanes which have one silicon removed from a corner of the T_8 cube. This T_7 structure commonly referred to as a trisilanol, posses both structural and electronic similarities to hydroxylated silica surface sites[9].

Polyhedral oligomeric silsesquioxane (POSS) are hybrid molecules of silicon and oxygen with similarities to both silica and silicone. POSS are condensed silicon - oxygen frameworks, which form random structures, ladder structures, cage structures and partial cage structures when the silicon atom is attached with an organic group[13]. POSS molecules with sizes of around 1nm in diameter can be thought of as the smallest particles of silica possible. POSS has a unique chemical composition, $SiO_{1.5}$, a hybrid which is an intermediate composition between that of silica SiO_2 and silicone SiO. The nature of the organic functional group determines compatibility with the polymer matrix. The organic group can be a simple alkyl, cycloalkyl or aryl, or reactive/ polymerizable groups such as acrylic, α-olefin, styrene, epoxide, carboxylic acid, isocyanate, amine, alcohol and silane, using such functionalization, the POSS structures can be either copolymerized with a range of monomers, or grafted onto polymer chains[14-15].

POSS molecules are physically of the same size with respect to polymer dimensions and nearly equivalent in size to most polymer segments and coils. POSS when mixed with virtually any ordinary polymer, bond to the organic molecules and to one another, forming large chains that weave through the polymer. The POSS chains act like nanoscale reinforcing fibers, producing extraordinary gains in heat resistance. Enhancements in the physical properties of polymers incorporating POSS segments result from POSS's ability to control the motions of the chains while still maintaining the processability and mechanical properties of the base resin. This is a direct result of POSS's nanoscopic size and its relationship to polymer dimensions.

Incompletely condensed silicon-oxygen frameworks contain reactive silanol functionalities. The reactivity of the silanol groups makes the POSS systems as models for silica supported catalysis. In a typical corner capping reaction, when the trisilanol and base are placed in a THF solution, slow addition of a trichlorosilane gave an excellent yield of product. This was found to be true for isobutyl POSS trisilanol, but was not the

ca
for
tris
tha

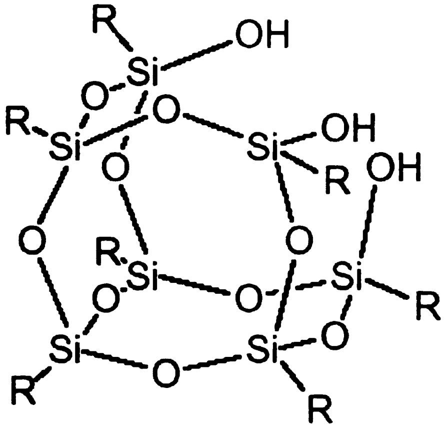
con
is k
reac
inter
espe

case for phenyl POSS trisilanol. Instead of a single product, several compounds were formed. The base used caused the problem by catalyzing the self-condensation of trisilanol phenyl POSS[1]. This is because of the higher acidity of trisilanol phenyl POSS than its aliphatic analogues[1].

The basis of our work is to study what effect does stable non-toxic phenyl group containing acidic systems have on the curing kinetics of the epoxy amine reaction since it is known that acidic alcohol systems like phenol accelerate the epoxy amine curing reaction. Recently with the availability of many nanoscale fillers, we were particularly interested in understanding the interaction between these fillers with polymer chains, especially phenyl acidic systems like trisilanol phenyl POSS.

Figure 1-1

Trisilanol Phenyl POSS



R = phenyl

$C_{42}H_{38}O_{12}Si_7$ MW: 931.34 g/mole

Soluble: tetrahydrofuran, chloroform, ethanol

Insoluble: hexane

Appearance: white powder

CHAPTER 2

MATERIALS AND SAMPLE CHARCTERIZATION

2.1 Materials

2.1.1 Epoxy Resins

Recent developments in polymer composite manufacturing have resulted in higher quality and lower cost epoxy systems. Epoxies are thermosetting materials that are used in a variety of applications including structural adhesives, coatings, and composites. Epoxy resin is defined as any compound containing two or more α- or 1,2- epoxy groups capable of being converted to a thermoset form or a three dimensional network structure. The curing of the epoxy resin is based on the reaction between the epoxide molecules themselves or the reaction between the epoxy group and the other types of reactive molecules with or without the presence of a catalyst. The former is referred to as homopolymerization, and the latter is an addition reaction, but both result in coupling as well as crosslinking. The curing process of a thermoset is governed by a competing relationship between the diffusion controlled and concentration controlled reaction, when the curing temperature is lower than the glass transition temperature the reaction is diffusion controlled. When the curing temperature is higher than the glass transition temperature, the reaction is concentration controlled. As the curing process proceeds, the network structure improves thereby increasing the glass transition temperature.

Epoxy resins are used for transfer molding, compression molding, injection molding, and reaction injection molding. The use of molded epoxy units has enjoyed a wide acceptance in the electrical and electronic industries. The reasons for use of epoxy molded compounds was because more reliable molding properties with a broader range of flows are available from epoxy compounds including batch to batch reproducibility. Also improved thermal shock resistance, permits the use of thinner wall sections, this offers not only less material usage but also better component packing density. The advantage of epoxy molding is the high production rates by virtue of short cycles, ease in handling of resins and minimal amount of cleanup. Also the molded parts offer surface finishes and overall appearance superior to most cast components. As compared to other thermosetting compounds epoxy molding compounds are readily usable for long-flow, low - pressure molding operations, faster cure by addition reactions without evolution of gaseous byproducts and a very low mold shrinkage, good adhesive bond to fillers and inserts, superior dimensional stability in the molded state, excellent electrical properties which are retained under high temperature and high humidity conditions and above all epoxy molded systems have excellent resistance to most acids, bases, solvents, salts, and other chemicals.

To reduce manufacturing costs many epoxy fiber composites are fabricated by using resin transfer molding (RTM). Transfer molding is a process where a solid material, in the form of powder or perform, is heated until it flows and is then transferred into a mold cavity containing the unit to be molded.

The choice of curing agents is a critical factor in controlling properties; it not only affects the properties of the cured resin, but also influences the rate of cure and the cure exotherm.

2.1.2 Curing Agents

The term curing is used to describe the process by which one or more kinds of reactants, i.e., and epoxide and curing agent, are transformed from low-molecular-weight materials to a highly crosslinked network. Epoxy resin curing agents can be divided into three technologically important classes: a) active hydrogen compounds, which cure by polyaddition reactions; (b) ionic initiators, which are subdivided into anionic and cationic; and (c) crosslinkers, which couple through the hydroxyl functionality of higher molecular weight bisphenol A type epoxy resins. In order to achieve desired engineering properties various curing agents, which react with the epoxy rings to form insoluble and intractable thermoset polymers, are used. For example, epoxy resins cured with anhydride based curing agents exhibit low viscosity, low exothermic heats of reaction, and little shrinkage when cured at elevated temperatures. The cured system exhibits good mechanical and electrical properties along with good thermal stability that makes the epoxy system useful in electrical applications.

Epoxy molecules linked together through the use of curing agents like amines, anhydrides, amides, etc form a three dimensional network. These network polymers at temperatures below their glass transition temperatures are hard intractable solids, but are rubbery above their glass transition temperature[16]. The characteristics of a network Epoxy depend on the functionality of the resin, flexibility of the epoxy chain, and the type and concentration of the crosslinking agent.

Although, in a broad sense, epoxy-curing agents are classed as catalytic, most cure by polyaddition reactions. Addition reaction is the most commonly used reaction for the cure of epoxy amines. The most widely used curing agents, based on such active hydrogen compounds as amines, acids, mercaptons, amides, and phenols undergo the additions via the active hydrogen and the terminal carbon atom of the epoxy group, with the subsequent conversion of the epoxy into a hydroxyl group.

These reactions are based on one active hydrogen in the curing agent per epoxy group, practical systems are not always based on this stoichiometry because of homopolymerization of epoxide or other side reactions, which may or may not be avoided. A significant amount of work has been reported in literature concerning the nature of reaction between epoxides and amines. The reactivity of amine and modified amines varies according to the steric hindrance in the neighborhood of the functional groups[5].

Several curing agents are used to cure epoxy resins out of which the most commonly used are amines. Both aliphatic and aromatic amines are used to cure epoxides. When aliphatic amines are blended with a epoxy resin they yield a mixture with a relatively short working life. They cure rapidly at room temperatures, and develop very high exothermic temperatures during the curing process. Cracking or even charring can result when a significant amount of epoxy resin is mixed and cured at one time. The physical and operating temperatures degrade rapidly as the operating temperatures increases. Aliphatic amine cured epoxies find their greatest use in small masses, where room temperature curing is desirable and operating temperatures are below 100^0C.

Aromatic amines cured epoxy systems have a considerably longer working life than that of aliphatic amine systems. These systems are operated at much higher temperatures and must be cured above 100^0C. They are less easy to work with than other curing agents because many are solids and must be melted into the epoxy. Some sublime when heated causing strains and residue deposition. Further there are certain catalytic cured epoxy systems which have longer working lives than the aliphatic amines but like the aromatic amines they require cures of 100°C or higher. Piperidine, boron trifluoride-ethylamine complex and benzyl dimethylamine are some of the catalytic curing agents used to cure epoxy resins.

Liquid acid anhydrides are easy to work with, blend easily with the resins, and reduce the viscosity of the resin. The working life of these systems is longer than that of aliphatic amine cured systems. However many acid anhydrides are solids and are mixed with epoxides at low temperatures giving pot lives as long as 10 days.

2.1.3 Promoter

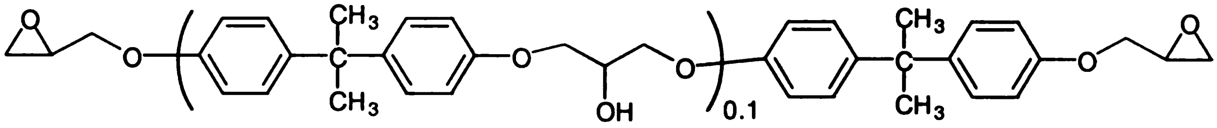
The ring opening reactions of the epoxies takes place by ionic mechanisms. The bond that is broken is the highly polar carbon-oxygen bond, which would be expected to break ionically. The reactions are generally carried out in polar solvents, such as the epoxy resin itself, and can be accelerated by adding polar agents. Under basic or neutral conditions, all ring opening reactions are essentially similar and involve the attack of nucleophile on one of the epoxide carbon atoms, as in the case of amine curing agent. A difference exists when the reaction is carried out under acidic conditions. Acids or electrophilic species because of the reversible formation of the more reactive conjugated acid of the epoxide, as in the case of Lewis acid like BF3, accelerates the addition of most nucleophiles considerably.

The effect of added compounds on the epoxy amine reaction decreases in the order: acids > phenols > water > alcohols > nitriles > aromatic hydrocarbons like benzene and toluene > dioxane > diidopropylether[4]. The acceleration of the epoxide amine reactions has been related to the ability of the accelerator to donate hydrogen bonds. The list of hydrogen donors, and therefore accelerators, included -OH, -COOH, $-SO_3H$, $-CONH_2$, -CONHR, $-SO_2NH_2$, and $-SO_2NHR$. Conversely hydrogen bond acceptors like -OR, -COOR, $-SO_3R$, $-CONR_2$, -CO, -CN, and $-NO_2$, retard the curing rate of the epoxy amine reaction. Acids are not used to accelerate the epoxy amine curing reaction because they form salts, but Lewis acids like BF_3 do promote the epoxy amine reaction.

2.2 Sample Materials

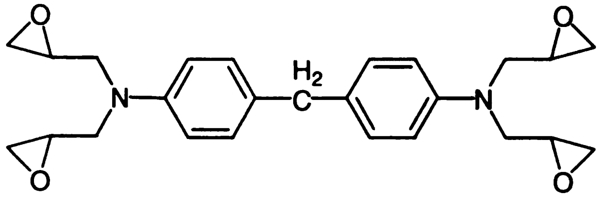
The epoxy resins used in this study contained 0 to 1 wt% fractions of trisilanol phenyl POSS. Two different conventional epoxy resins are used in this study. The first one is a diglycidyl ether of Bisphenol A, DGEBA (Dow Chemical DER 332), and the second is tetraglycidyl diamino diphenyl methane, TGDDM (Aldrich Chemicals). Two curing agents were used for each of the epoxy resins, one is a diamine terminated polypropylene oxide; Jeffamine D230 (Huntsman Chemicals), and the other was 2,Methyl 1,5 pentadiamine; Dytec A (DuPont Chemicals). The chemical structures of the components are described in Figure 2-1 through Figure 2-4.

Figure 2-1



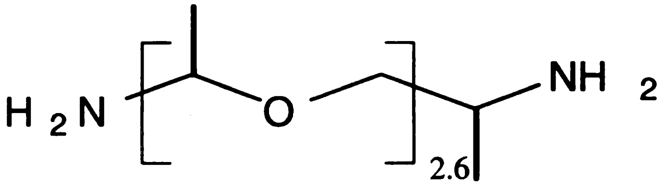
Diglycidyl Ether of BisphenolA

Fig 2-2



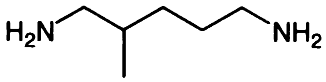
Tetra Glycidyl Diamino DiPhenyl Methane

Fig 2-3



Jeffamine D-230

Fig 2-4



DytecA

2.3 Sample Preparation

The epoxy resins used in this study contained 0 to 1 wt% fractions of trisilanol phenyl POSS. Two different conventional epoxy resins are used in this study. The first one is a diglycidyl ether of Bisphenol A, DGEBA (Dow Chemical DER 332), and the second is tetraglycidyl diamino diphenyl methane, TGDDM (Aldrich Chemicals). Two curing agents were used for each of the epoxy resins, one is a diamine terminated polypropylene oxide; Jeffamine D230 (Huntsman Chemicals), and the other was 2,Methyl 1,5 pentadiamine; Dytec A (DuPont Chemicals).

The DGEBA epoxide monomer was first preheated at 50^{0}C for 30 minutes to melt any crystals present. First, trisilanol phenyl POSS and DGEBA were mixed together and stirred by hand. Then the equivalent of hydrogen of the curing agent (Jeffamine D230 or Dytec A) is added to the equivalent of epoxy present and then the mixture is stirred by mechanical means. The weights of each component in the sample mixture are tabulated in Table 2-1 through Table 2-5. The mixture was then degassed in vacuum for 10 minutes at room temperature. The mixture was poured in a mold and cured in an air oven at 100^{0}C for 12 hours, and then slowly cooled in the oven overnight to room temperature. Here the oven was initially preheated to the curing temperature and then the mold was placed in the air oven.

For the TGDDM the same process as above was adopted but the curing was done at 150^{0}C for 12 hours. The most important point in the preparation of the sample is that the trisilanol phenyl POSS is first added into the epoxy resin and later the curing agent amine is added to the epoxy trisilanol phenyl POSS system.

The epoxy samples are cut into rectangular specimens and stored in a desiccator at room temperature. These samples were used to perform Dynamic Mechanical Analysis (DMA) experiments.

Table 2-1

DGEBA - Jeffamine D 230 cured at 100^{0}C

Epoxy (g)	Amine (g)	POSS (g)	%POSS
9.851	3.500	0.000	0.0
25.362	8.787	0.068	0.2
27.695	9.594	0.150	0.4
16.861	5.840	0.137	0.6
11.663	4.054	0.127	0.8
11.508	3.989	0.157	1.0

Table 2-2

DGEBA – DytecA system cured at 100^0C

Epoxy (g)	Amine (g)	POSS (g)	%POSS
19.517	3.412	0.000	0.0
17.264	3.016	0.048	0.2
16.184	2.827	0.076	0.4
16.897	2.974	0.120	0.6
17.792	3.114	0.168	0.8
18.052	3.161	0.214	1.0

Table 2-3

TGDDM – Jeffamine D 230 cured at 150^{0}C

Epoxy (g)	Amine (g)	POSS (g)	%POSS
8.736	4.755	0.000	0.0
22.892	12.469	0.073	0.2
20.181	10.994	0.125	0.4
13.859	7.544	0.129	0.6
18.690	10.185	0.233	0.8
32.104	17.478	0.504	1.0

Table 2-4

TGDDM-DytecA system cured at 150^0C

Epoxy (g)	Amine (g)	POSS (g)	%POSS
16.738	4.595	0.000	0.0
17.275	4.743	0.044	0.2
14.342	3.938	0.073	0.4
17.748	4.873	0.136	0.6
17.230	4.730	0.177	0.8
15.450	4.242	0.199	1.0

Table 2.5

TGDDM-DytecA system cured at 100^0C

Epoxy (g)	Amine (g)	POSS (g)	%POSS
12.676	3.478	0.000	0.0
11.535	3.167	0.059	0.4
13.569	3.724	0.175	1

CHAPTER 3

MECHANICAL PROPERTIES OF EPOXY NETWORK GLASSES CONTAINING TRISILANOL PHENYL POSS

3.1 Dynamic Mechanical Analysis

Dynamic Mechanical Analysis of polymeric solids is one of the most effective and practical methods of studying the relationship between polymeric structure and product performance. The viscoelastic measurements over the entire significant temperature range provide information on the usefulness of a material as determined by the temperature dependence of its stiffness. From the corresponding mechanical loss data, the internal transition behavior of the material can be studied.

Amorphous polymers are polymers having non-crystalline structure. Amorphous polymers may have some molecular order but usually are substantially less ordered than crystalline polymers and subsequently have inferior mechanical properties. Materials in this class do not have detectable melting point. Glass transition temperature is the result of the breakdown of amorphous region.

The Glass Temperature is defined as the temperature range at which an amorphous polymer (or the amorphous regions in a semi-crystalline polymer) changes from a hard and relatively brittle condition to a viscous or rubbery condition. The glass transition temperature is the temperature at which the material properties change from those of a plastic to those of a rubber; this is a characteristic property of each substance. The coefficient of expansion of a substance undergoes a more abrupt change in the region of glass transition. The temperature at this change is defined as the glass transition temperature. The temperature dependence upon cooling of the specific volume is determined by a suitable technique and the temperature at the change in slope is taken as the glass transition temperature T_g. In this temperature region, many physical properties such as hardness, brittleness, thermal expansion, and specific heat undergo rapid changes. Coefficient of Thermal Expansion (CTE) and Specific Heat of the polymer increases when heated through the glass temperature T_g, but the Elastic Modulus decreases.

In Dynamic Mechanical Analysis the instrument applies a sinusoidal mechanical strain deformation to the sample specimen. It measures four quantities: specimen temperature, load (or stress), probe position (or strain), and time (or phase angle, δ).

The cured epoxy samples are cut into rectangular specimens for the DMA experiments. The specimens are examined using a Rheometric Scientific Solids Analyzer RSA III. The test samples have a span length of 25mm long. All the samples were approximately of 12mm width and 2mm thickness. The sample dimensions are measured and the specimen is loaded into the RSAIII. Three point bending supports a solid rectangular sample in horizontal position. The sample ends rest on the motor, while the transducer applies load to the center of the sample. The sample is bent around the fulcrum held by the transducer where the transducer applies a small amount of static bending force. The sample is therefore tested under a static bending mode. The sample is placed on the lower tool fixture of the three point beam and by adjusting the stage position to bring the fulcrum to the sample, the fulcrum is allowed to touch the sample with minimum amount of load, this provides a zero reference point throughout the test and also ensure that the bearing overload warning is not displayed. The load of 100g was initially applied on the sample at zero time and the test is started and the dynamic Elastic (Storage) Modulus E' and the tangent of the phase angle shift between stress and strain, tanδ were determined. The test performed is a constant strain rate, constant frequency temperature ramp test in three point bending mode. In all the cases a bending oscillation of 2πrad/s was used while heating at a temperature rate of 1^0C/min for a strain rate of 0.02%. The measurements were carried out from room temperature to 100^0C for all DGEBA/Jeffamine D-230 samples and up to 150^0C for DGEBA/DytecA and up to 250^0C for the TGDDM samples. The glass transition temperature is determined from the tanδ curve. It is taken to be the temperature of the peak of the tanδ curve.

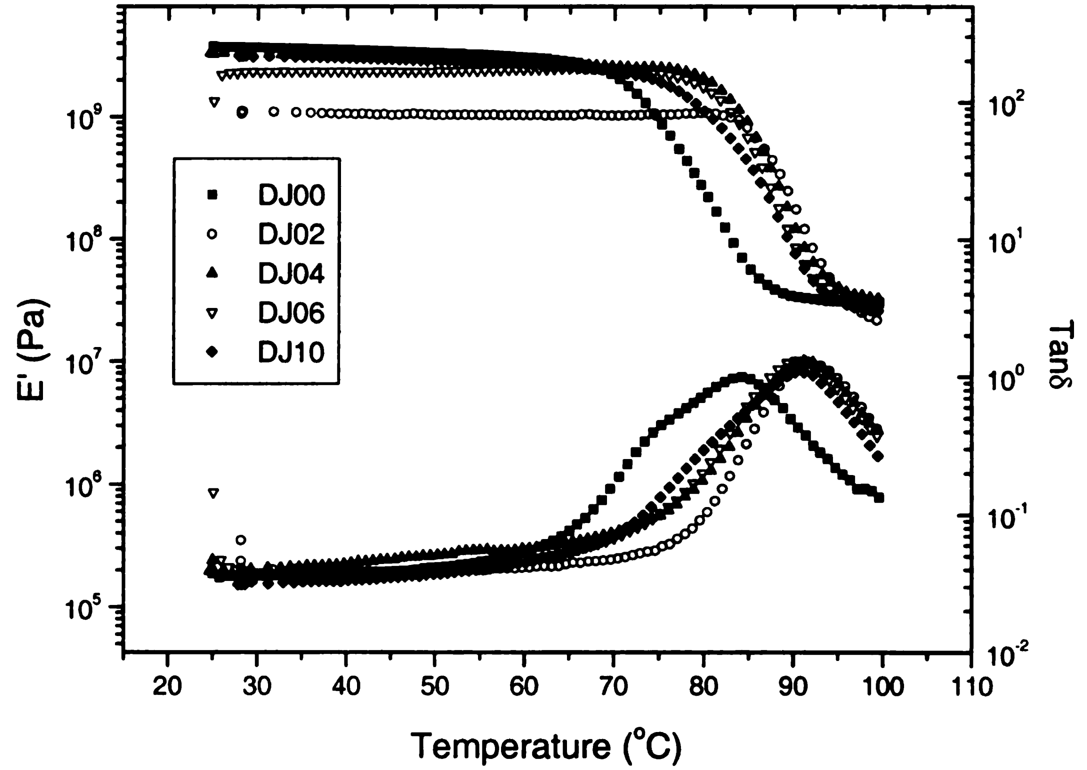
3.2 Results and Discussion

3.2.1 DGEBA-Jeffamine D 230 cured at 100^{0}C for 12 hours

DMA curves of DGEBA epoxy resins having varying amounts of trisilanol phenyl POSS and cured with Jeffamine D-230 are shown in Figure 3-1. This is nearly, a completely cured system since the curing temperature is greater than the glass transition temperature $T > T_g$, the curing reaction is concentration controlled for temperatures below the T_g but it is diffusion controlled for temperatures above T_g. Figure 3-1 clearly shows that the Glass Transition temperatures of the DGEBA/Jeffamine D-230/trisilanol POSS samples are slightly higher than those of the neat DGEBA/Jeffamine D-230 sample. The glass transition temperature is determined from the tanδ curve. It is the temperature of the peak of the tanδ curve. The T_g values of the DGEBA/Jeffamine D-230 samples with POSS composition varying by 0.2% from 0% to 1% are summarized in Table 3-1. The increase of about 6^{0}C is observed in samples containing trisilanol phenyl POSS compared to the sample not containing POSS. This indicates that there is an improved network formed in the case of samples containing POSS. Since the curing time is only 12 hours, it can be said that the curing reaction is accelerated to form a better networked system by trisilanol phenyl POSS in the case of samples containing POSS. Dusek et al.[17] found that the only reaction that occurred during the epoxy/amine reaction when a phenol or an acid is present is the addition of the amino hydrogen to epoxy groups. Oshiro, Komori, and coworkers[18-20] and Harrod[21] reported that there is an unequal activity between the amine functions and also reported that the primary amine and the generated secondary amine had different reactivities toward the epoxy group[24]. The presence of phenol in an acidic environment initially improves the rate of the secondary amine reaction with the epoxy leading to an increased consumption of amine and epoxy, thereby forming a better network.

To further investigate the effect of trisilanol phenyl POSS in epoxy amine systems a more basic amine, DytecA than Jeffamine D 230 is chosen and DGEBA is cured with DytecA. DytecA was used to study the effect of the basic amine curing agents on the promotional activity of trisilanol phenyl POSS.

Figure 3-1 DMA results of DGEBA epoxy resin with Jeffamine D-230



DJ00 = DGEBA/Jeffamine D230/0% trisilanol phenyl POSS; DJ02 = DGEBA/ Jeffamine D230 /0.2% trisilanol phenyl POSS; DJ04 = DGEBA/ Jeffamine D230/0.4% trisilanol phenyl POSS; DJ06 = DGEBA/ Jeffamine D230 /0.6% trisilanol phenyl POSS; DJ08 = DGEBA/ Jeffamine D230 /0.8% trisilanol phenyl POSS; DJ10 = DGEBA/ Jeffamine D230 /1.0% trisilanol phenyl POSS

Table 3.1

Epoxy: DGEBA Amine: Jeffamine D-230

POSS: Trisilanol Phenyl-POSS

POSS wt%	Tg DMTA (ΔT)*
0%	84.2(12)
0.20%	92.1(10)
0.40%	91.2(9)
0.60%	90.6(9)
0.80%	91.6(10)
1.00%	91.7(12)

- Tg is determined by using tanδ curve, ΔT is the temperature range at full width and at half height of the tanδ peak

3. 2.2 DGEBA – DytecA cured at 100^{0}C for 12 hours

To study the effect of using a stronger basic amine on the curing reaction, DytecA (pH=12.1) is used to cure the DGEBA epoxy resin containing varying amounts of trisilanol phenyl POSS. The DMA curves for DGEBA epoxy trisilanol POSS with DytecA as curing agent are shown in Figure 3-2. Here, there is an appreciable increase in T_g for samples with POSS compared to that of sample without POSS. The T_g values are listed in Table 3-2. In the DytecA cured DGEBA epoxy systems, the low T_g of the neat epoxy sample can be attributed to some unreacted functional groups that lower the crosslinking density in the sample, but the point to be taken note of in here is that all the samples with different POSS loading have nearly the same glass transition temperatures T_g. The near overlap of the DMA curves of 0.6% POSS and 0.8%POSS samples in Figure 3-2 is a clear indication that the higher T_g has nothing to do with the POSS grafting into the epoxy resin and also hydrogen bonding can be ruled out since the observed T_g increase with and without POSS in the case of DGEBA and DytecA was nearly 24^{0}C for only 1.0% trisilanol phenyl POSS, which is not possible by pure hydrogen bonding. Since the system is cured below its T_g, it is clear that the system without trisilanol phenyl POSS is under cured and the curing reaction is diffusion controlled. The higher T_g values of the epoxy samples containing trisilanol phenyl POSS validate the point that trisilanol phenyl POSS promotes additional curing in the later stages when the curing mechanism is diffusion controlled.

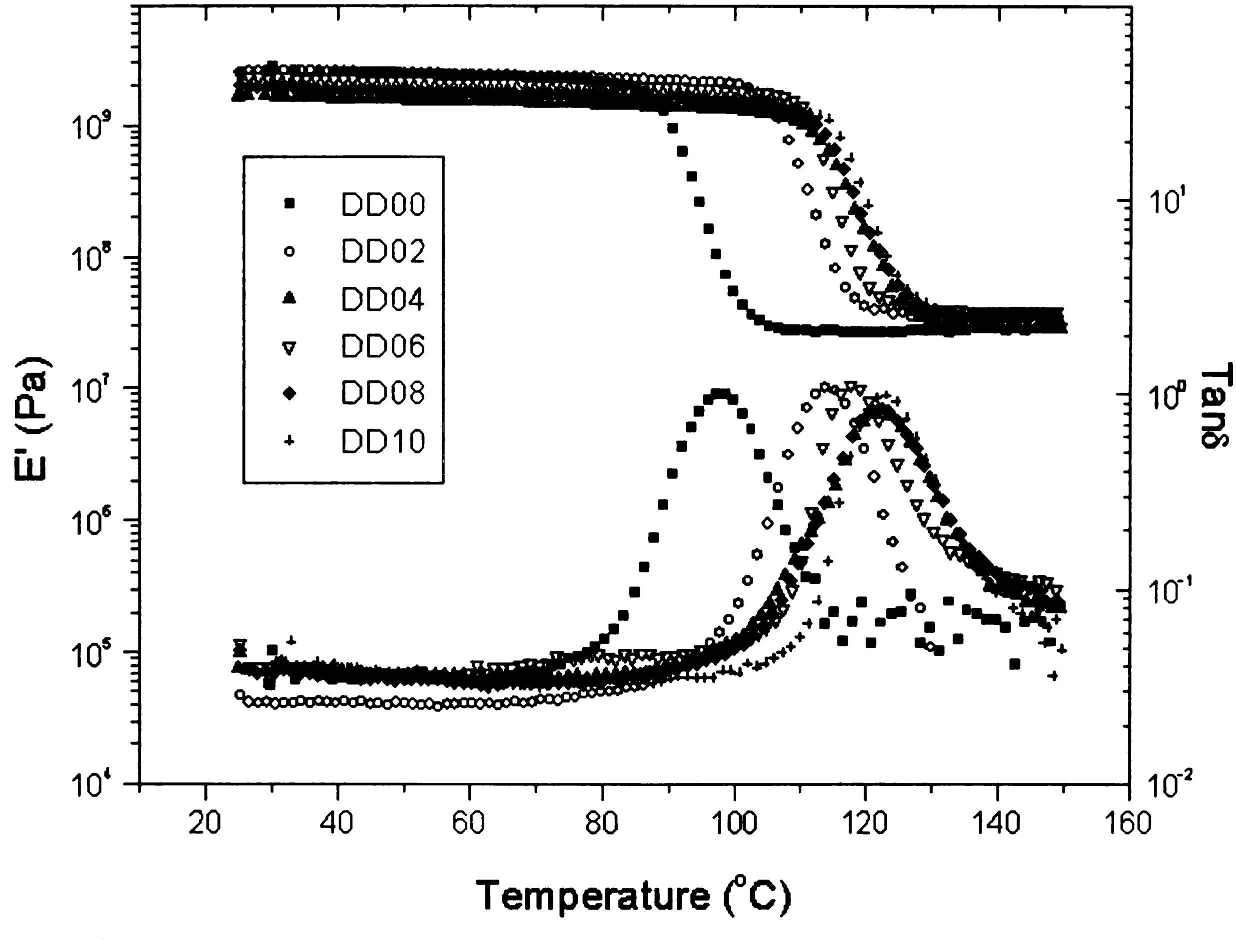
The Storage Modulus (E') curves for the DGEBA-DytecA are shown in Figure 3. The Storage Modulus (E') in the rubbery region for the DGEBA-DytecA systems shows

an increase for samples containing trisilanol phenyl POSS. Since the rubbery plateau modulus is directly proportional to the crosslinking density. Increase in the modulus indicates a higher degree of crosslink, which is the reason why trisilanol phenyl POSS containing epoxy samples have a better T_g compared to neat epoxy samples. This shows that trisilanol phenyl POSS promotes the curing reaction between the epoxy and the amine.

A higher T_g value for DGEBA/trisilanol phenyl POSS system is observed with DytecA compared to Jeffamine D-230 because DytecA (pH=12.1) is a stronger basic amine than Jeffamine D-230 (pH=11.7). NMR studies clearly show that DytecA is a stronger amine than Jeffamine D 230.

To verify the above results with a different epoxy resin, a better cross-linking epoxide having high temperature end applications was chosen. The epoxy resin used was tetraglycidyl diphenyl diamino methane (TGDDM). Since TGDDM has four epoxy groups compared to two for DGEBA and nearly the same middle chain, an improved network is expected for TGDDM amine systems, so the T_g for the TGDDM amine systems will be much higher than that of DGEBA amine systems. The TGDDM amine systems are cured at a higher temperature than the DGEBA amine systems.

Figure 3-2 DMA results of DGEBA epoxy resin with DytecA



DD00 = DGEBA/DytecA/0% trisilanol phenyl POSS; DD02 = DGEBA/DytecA /0.2% trisilanol phenyl POSS; DD04 = DGEBA/DytecA /0.4% trisilanol phenyl POSS; DD06 = DGEBA/DytecA /0.6% trisilanol phenyl POSS; DD08 = DGEBA/DytecA /0.8% trisilanol phenyl POSS; DD10 = DGEBA/DytecA /1.0% trisilanol phenyl POSS

Table 3.2

Epoxy: DGEBA Amine: DytecA

POSS: Trisilanol Phenyl-POSS

POSS wt%	Tg DMTA (ΔT)*
0%	98.00(10)
0.20%	109.29(13)
0.40%	121.95(9)
0.60%	118.06(8)
0.80%	121.73(9)
1.00%	123.13(9)

- Tg is determined by using tanδ curve, ΔT is the temperature range at full width and at half height of the tanδ peak

3.2.3 NMR Data of Trisilanol Phenyl POSS with Jeffamine D-230 and DytecA

The NMR plots of trisilanol phenyl POSS with Jeffamine D-230 and DytecA are shown in Figures 3-3 and Figure 3-4 respectively. Dr. Haddad T.S. of Hybrid Plastics has done the NMR experiments. The effect of Jeffamine D-230 on trisilanol phenyl POSS can be clearly seen in Figure 3-3. At time t = 15minutes a decrease in the Ph_8T_8 peak is observed which implies that the POSS cages are being descrambled but the effect is slow. Since there is still a small peak it can be said that Jeffamine D-230 will finally completely descramble the POSS structure over time. After 75minutes a decrease in the phenyl triol peak is observed with a crystalline substance forming on the NMR tube.

The effect of DytecA can be seen in Figure 3-4. After time t = 15 minutes we see the POSS cages completely descramble, the phenyl triol peak completely disappears. This is possible due the high basicity of the amine used. From the NMR data it can be said that the phenyl triol (the acidic group which accelerates the epoxy/amine curing reaction) lasts longer in the case of Jeffamine D-230 than in Dytec A.

From the NMR results we observe that the trisilanol phenyl POSS completely descrambles the POSS cages in 15 minutes forming a rigid linear chain polymer. The rigid polymer still contains the -OH groups, which are readily available for improving the secondary amine reaction, which result in an improved network.

In the case of Jeffamine D230 the amine takes a longer time to descrambles the POSS cages, which shows that DytecA is a stronger amine than Jeffamine D230.

Figure 3-3 NMR spectra of trisilanol phenyl POSS in Jeffamine D 230

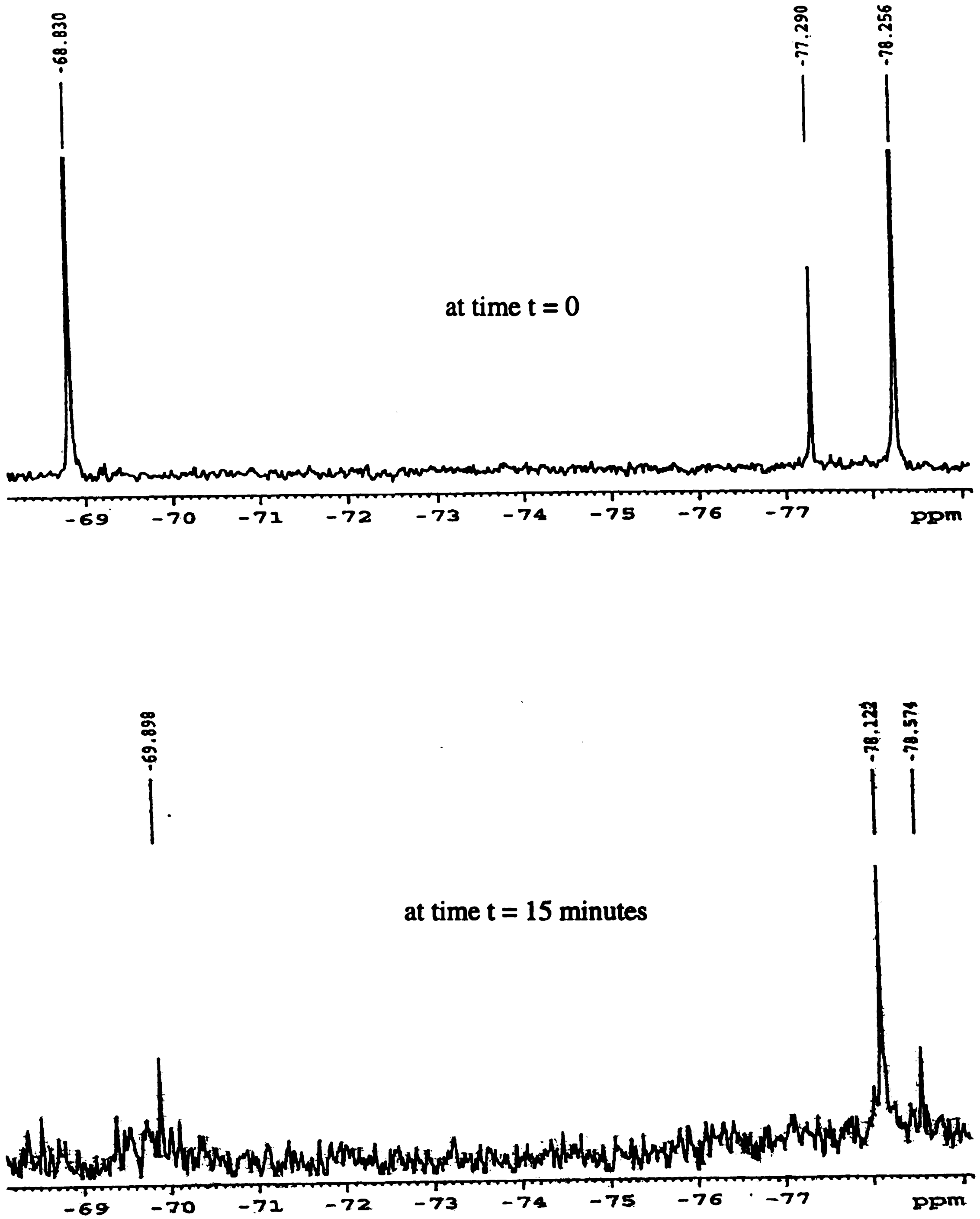
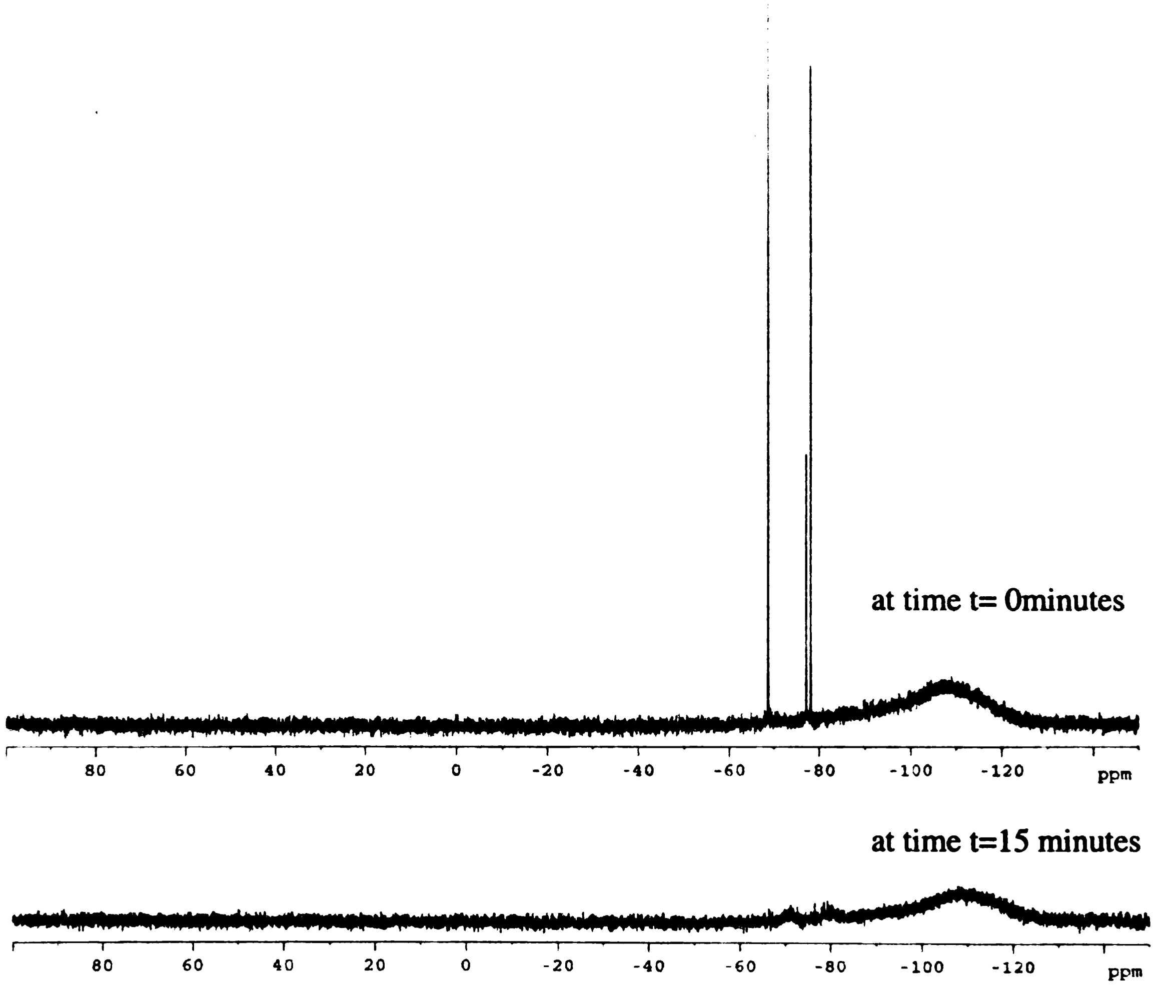


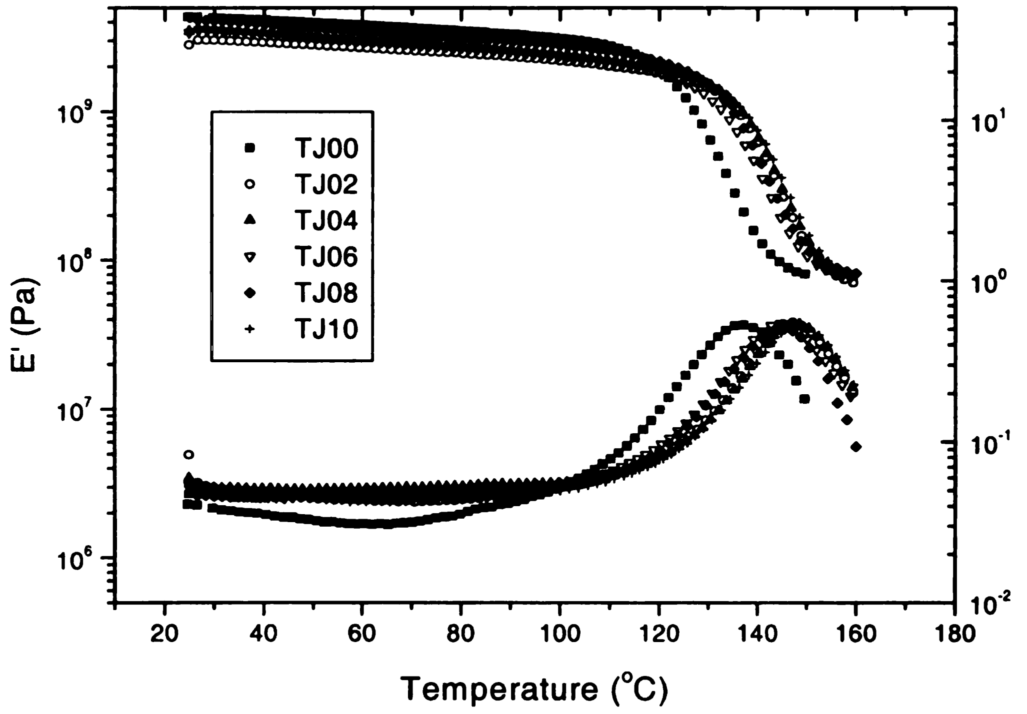
Figure 3-4 NMR spectra of trisilanol phenyl POSS in DytecA



3.2.4 TGDDM-Jeffamine D-230 cured at 150^{0}C for 12 hours

Changing the epoxy resin to improved network forming epoxy resin like TGDDM enhanced T_g improvement can be observed for TGDDM amine systems, as seen in Figure 3-5. The T_g values are listed in Table 3-3. The epoxy amine system is cured at a temperature above its T_g so the epoxy network formed is nearly a complete cured system, though an increase of about 12^{0}C is observed for samples with trisilanol phenyl POSS, this may only be to the less curing time employed for curing the epoxy systems where the trisilanol phenyl POSS promoted the curing reactions when the curing reaction is diffusion controlled for samples containing POSS thus leading to differences in glass transition temperatures T_g between samples with and without trisilanol POSS. Also there are no considerable differences in the Storage Modulus (E') values for $T < T_g$. The difference between the epoxy systems cured with Jeffamine D-230 are that they are cured at temperatures higher than their glass transition temperatures T_g and the other systems cured with DytecA have a much lower curing temperature much below their glass transition temperatures T_g. The increase of 12^{0}C is justified because of the more rigid TGDDM Jeffamine D230 system.

Figure 3-5 DMA results of TGDDM epoxy resin with Jeffamine D-230



TJ00 = TGDDM /Jeffamine D230/0% trisilanol phenyl POSS; TJ02 = TGDDM / Jeffamine D230/0.2% trisilanol phenyl POSS; TJ04 = TGDDM / Jeffamine D230/0.4% trisilanol phenyl POSS; TJ06 = TGDDM / Jeffamine D230/0.6% trisilanol phenyl POSS; TJ08 = TGDDM / Jeffamine D230/0.8% trisilanol phenyl POSS; TJ10 = TGDDM / Jeffamine D230/1.0% trisilanol phenyl POSS

Table 3.3

Epoxy: TGDDM

Amine: Jeffamine D-230

POSS: Trisilanol Phenyl POSS

POSS%	Tg DMTA (ΔT)*
0%	136.8(16)
0.20%	146.5(17)
0.40%	148.8(16)
0.60%	144.2(18)
0.80%	145.0(16)
1.00%	148.4(17)

- Tg is determined by using tanδ curve, ΔT is the temperature range at full width and at half height of the tanδ peak

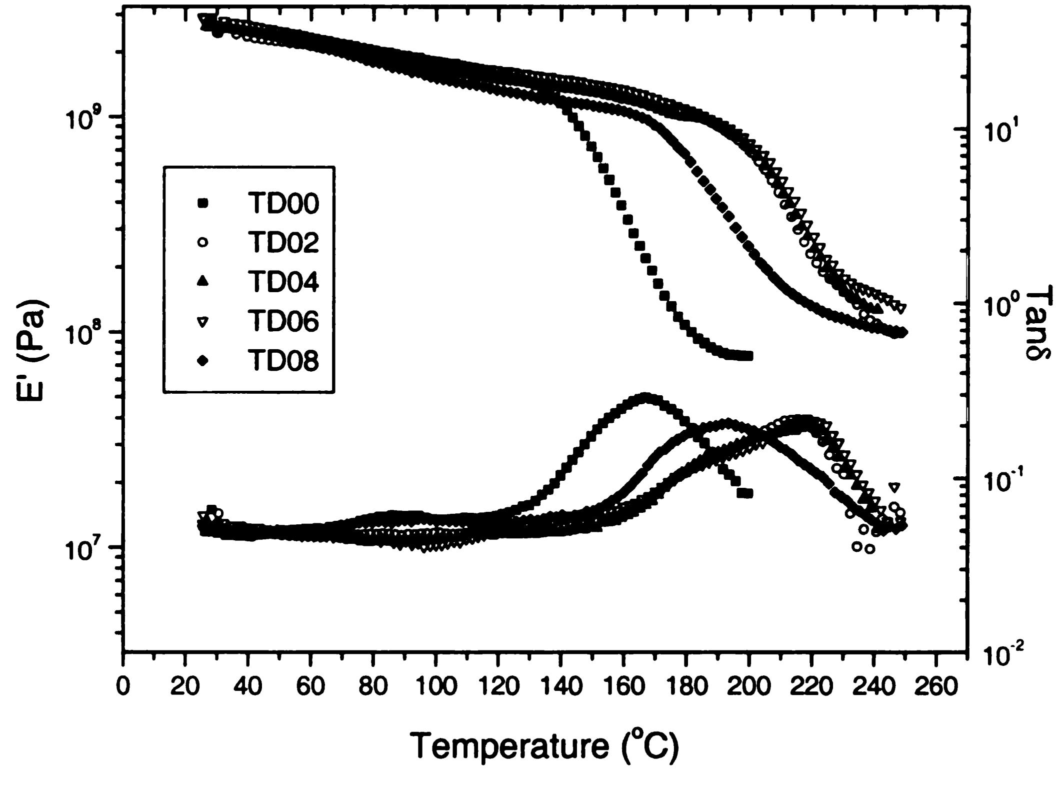
3.2.5 TGDDM-DytecA cured at 150^{0}C for 12 hours

To observe notable changes in the glass transition temperatures the TGDDM epoxy resin is cured with the more basic amine DytecA. The samples are under cured to study the effect of trisilanol phenyl POSS on the curing kinetics of the TGDDM DytecA system. The DMA curves are shown in Figure 3-6 and the glass transition temperatures are tabulated in Table 3-4. As expected a notable increase in T_g of about 40^{0}C is observed. It is well known that epoxy resin shows a large tanδ peak in the glass transition region. However the area of the tanδ peak decreased on the addition of trisilanol phenyl POSS into the epoxy resin. This suggests that the trisilanol phenyl POSS is nearly dispersed in the epoxy resin and motion of the network is strongly restricted by the formation of a better network. From the NMR graphs it can be said that POSS descrambles to form linear chain polymers. These polymers contain rigid –OH groups that improve the secondary amine reaction rate thus improving the network formation by the diffusion controlled mechanism of the curing reaction of TGDDM and DytecA.

Though initially the concentration controlled curing reaction occurs for low T_g networks, that is when the mobility of the network is more, at a later stage the diffusion controlled mechanism dominates the curing mechanism in network formation leading to improved networks. An important point that was observed for the case of epoxy amine systems containing POSS was that in parallel experiments conducted exactly at the same experimental conditions showed consistent results which was not the case for epoxy amine systems without trisilanol POSS. This was observed only for the epoxy amine systems where the amine was DytecA.

Figure 3-6

DMA results of TGDDM epoxy resin with DytecA cured at 150^{0}C for 12 hours



TD00 = TGDDM /DytecA/0% trisilanol phenyl POSS; TD02 = TGDDM /DytecA/0% trisilanol phenyl POSS; TD04 = TGDDM /DytecA/0% trisilanol phenyl POSS; TD08 = TGDDM /DytecA/0% trisilanol phenyl POSS

Table 3.4

Epoxy: TGDDM Amine: DytecA

POSS: Trisilanol Phenyl-POSS

POSS wt%	Tg DMTA (ΔT)*
0%	166.99(25)
0.20%	214.11(16)
0.40%	220.29(20)
0.60%	219.18(19)
0.80%	192.93(28)
1.00%	212.81(15)

- Tg is determined by using tanδ curve, ΔT is the temperature range at full width and at half height of the tanδ peak

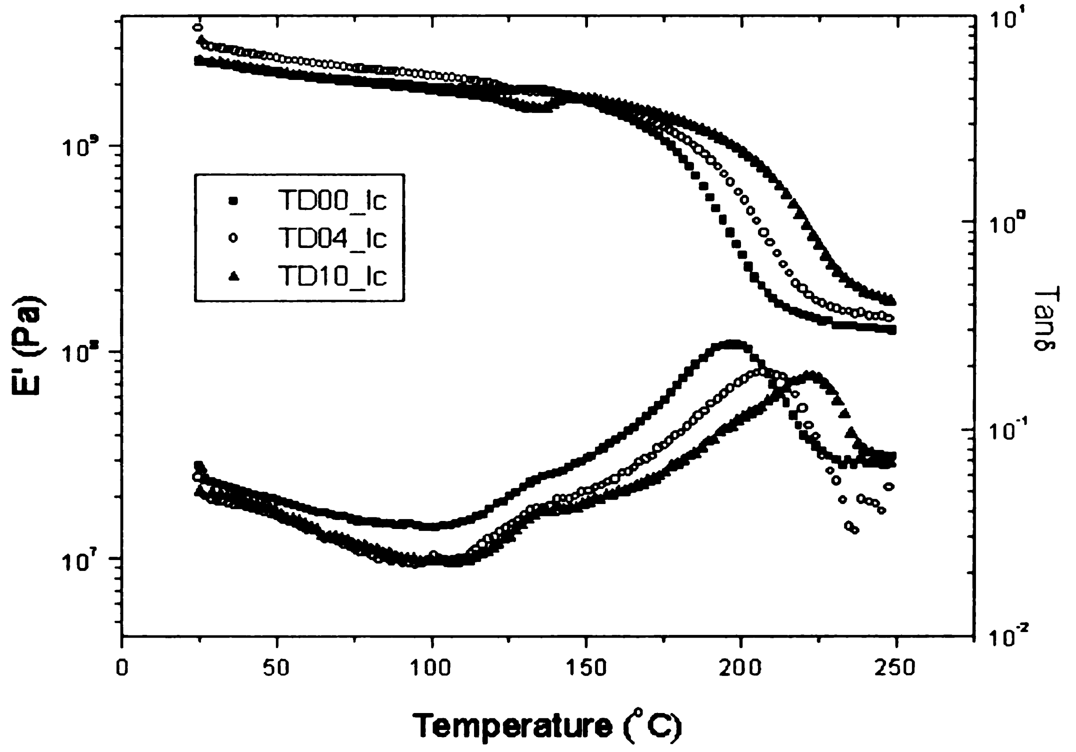
3.2.6 TGDDM-DytecA cured at 100^0C for 24 hours

Now we made another set of samples of TGDDM using DytecA as curing agent and cured them at 100^0C for 24 hours. DMA analysis on these samples is shown in Figure 3-7. The glass transition temperatures T_g observed are tabulated in Table 1. We observe a small peak at nearly 135^0C in the tanδ curve for the DMA curves, this shows an additional cure taking place, which is possible since the heating rate is only 1^0C/minute and the curing temperature for the samples was far less than the glass transition temperature T_g. The glass transition temperature T_g of the neat TGDDM/DytecA decreased when compared to the glass transition temperature T_g of neat TGDDM/DytecA cured at 150^0C for 12 hours, this clearly shows that the system is uncured, but the TGDDM/DytecA containing trisilanol phenyl POSS (1.0%) showed the same results in both the cases. This indicates that POSS has accelerated the curing reaction in the case of the POSS containing epoxy amine samples and a much lower temperature is required for the curing of the epoxy resin using an amine.

The above DMA results shows that the presence of a small amount of POSS could significantly increase the T_g of neat epoxy resin at low curing temperatures, because the addition of 0.2% is not likely to increase the viscosity of the epoxy resins, it is thus of importance to the POSS application in low temperature curing process.

Figure 3-5

DMA results of TGDDM epoxy resin with DytecA cured at 100⁰C for 24 hours



TD00_lc = TGDDM /DytecA/0% trisilanol phenyl POSS at low temperature cure; TD04_lc = TGDDM /DytecA/0.4% trisilanol phenyl POSS at low temperature cure; TD10_lc = TGDDM /DytecA/1.0% trisilanol phenyl POSS at low temperature cure.

Table 3.5

Epoxy: TGDDM Amine: DytecA

POSS: Trisilanol Phenyl-POSS

POSS wt%	Tg DMTA (ΔT)*
0%	198.17(20)
0.40%	210.07(21)
1.00%	222.70(16)

- Tg is determined by using tanδ curve, ΔT is the temperature range at full width and at half height of the tanδ peak

CHAPTER 4

FOURIER TRANSFORM INFRARED SPECTROSCOPY

4.1 Introduction

Fourier Transform Infrared Spectroscopy is an important technique to identify the presence of certain functional groups in a molecule. Fourier Transform Infrared Spectroscopy (FTIR) measures dominantly vibrations of functional groups and highly polar bonds. FTIR spectrometers record the interaction of infrared (IR) radiation with experimental samples, measuring the frequencies at which the sample absorbs the radiation and the intensities of the absorptions. Since chemical functional groups are known to absorb light at specific frequencies, determining these frequencies allows identification of the sample's chemical makeup. FTIR experiments generally can be classified into two categories; one is qualitative analysis where the aim is to identify the sample and the other is quantitative analysis of the intensity of an absorption (or more commonly absorptions), which is directly related to the concentration of the component

4.2 Experimental Procedure

Fourier transform infrared spectroscopy (FTIR) was used to monitor the curing kinetics of epoxy resins. In each experiment, samples were cast into thin films on FTIR cards (polyethylene) after immediately mixing the equivalent weights of epoxide and amine. These FTIR cards were placed in an oven at desired temperatures, and they were subjected to FTIR scans periodically during the experiments. FTIR spectra were obtained using a Bio-Rad FTS3000. Each spectrum represents the average of 68 scans.

4.3 Results and Discussion

FTIR was used to study the curing kinetics of two systems: DGEBA with DytecA, and TGDDM with DytecA. Figure 4-1 shows the FTIR spectra of sample DGEBA/DYTECA/0.4%POSS cured at 60°C. The detailed peak assignment can be found in the literature [ref]. In this study, we used the aromatic C=C stretching peak (1510 cm^{-1}) as an internal standard. We note that because the POSS molar ratio was very small in the sample DGEBA/DYTECA/0.4% POSS, the contribution of the phenyl groups in the POSS is negligible due to the high molecular weight of trisilanol phenyl POSS. The peak at 914 cm^{-1} was used to calculate the consumption rate of epoxide. As seen, the peak intensity of epoxide obviously decreased in the curing process. However, there was still a significant epoxide peak even after 1020 min. This is because the chosen curing temperature in this experiment was much lower than the T_g (typically at 90°C) of the epoxy resin. Therefore, the conversion of epoxide is lower. The etherification peak (1070 cm^{-1}) was found to be insignificant in both DGEBA/DYTECA/0%POSS and DGEBA/DYTECA/0.4%POSS samples. Thus, the presence of POSS did not promote the etherification of DGEBA, and the etherification effect can be neglected in this study. Hydroxyl group at 3450 cm^{-1} was observed in both DGEBA/DYTECA/0%POSS and DGEBA/DYTECA/0.4%POSS samples. Since the contribution of silanol group is low because of its low molar ratio, the hydroxyl peak should be due to the backbone of the epoxy resin that contains the hydroxyl group. The intensity of hydroxyl group showed barely observable increase in sample DGEBA/DYTECA/0.4%POSS despite the fact that it showed significant T_g improvement than sample DGEBA/DYTECA/0%POSS. It is

Figure 4-1 FTIR results of DGEBA epoxy resin with DytecA

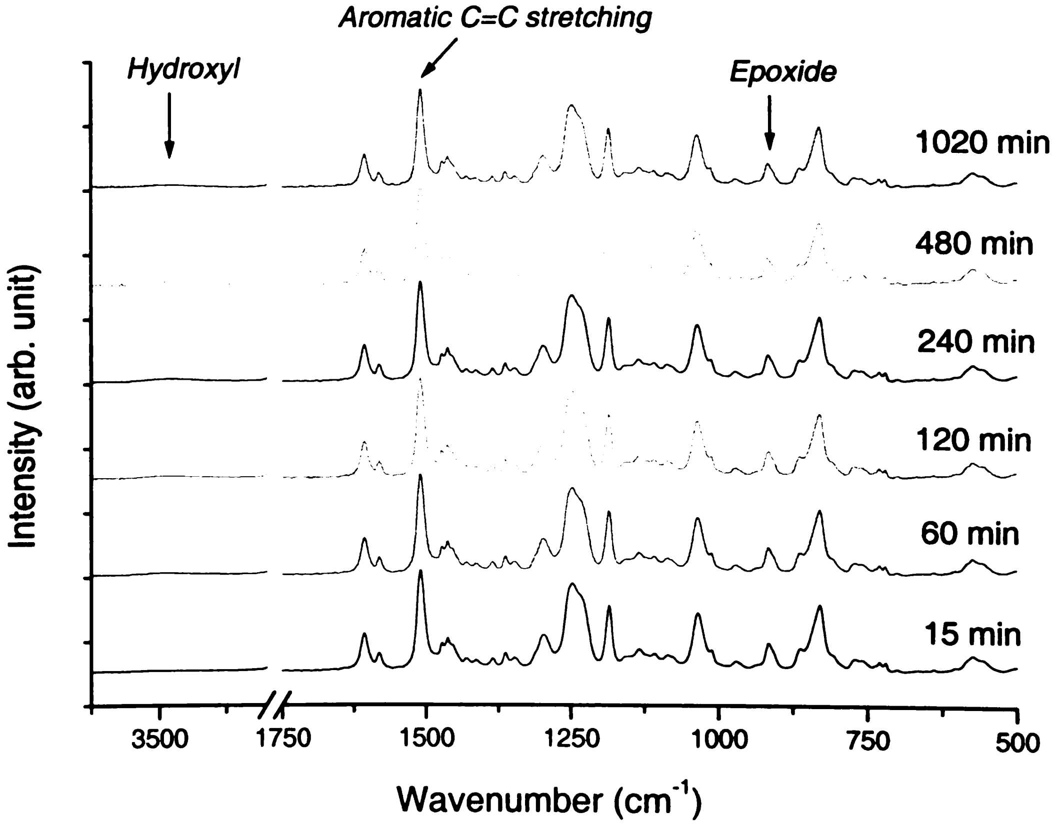
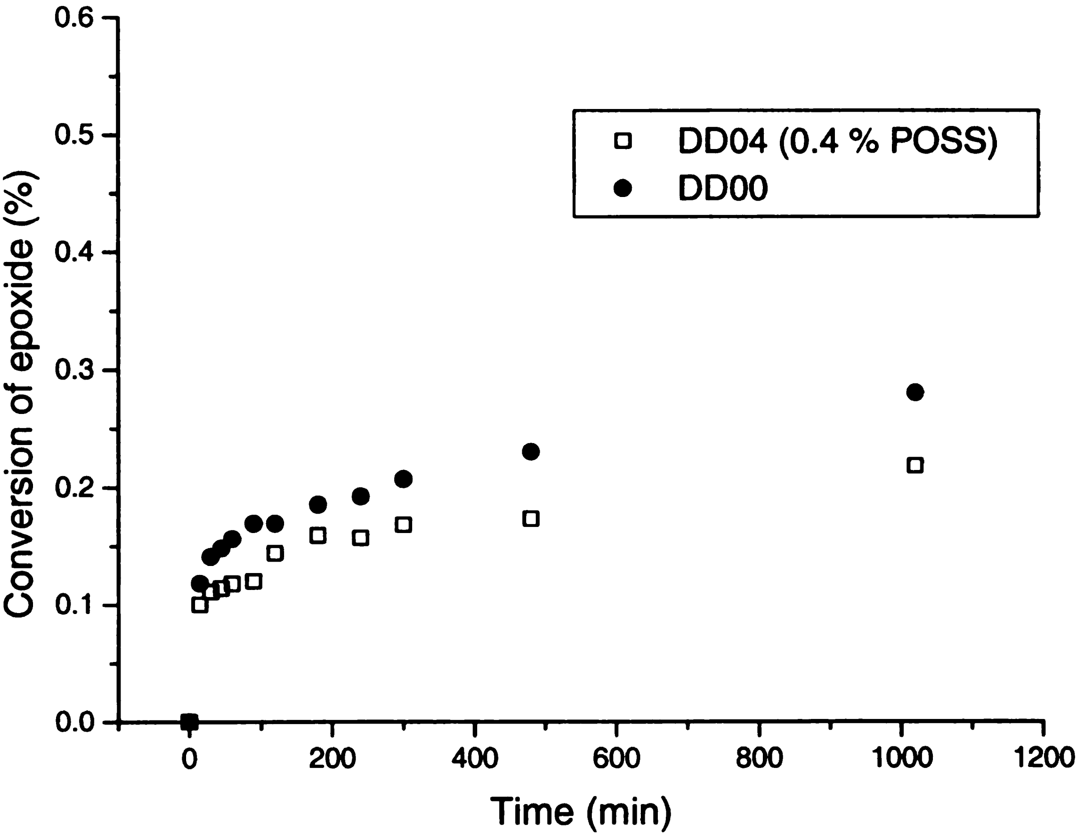


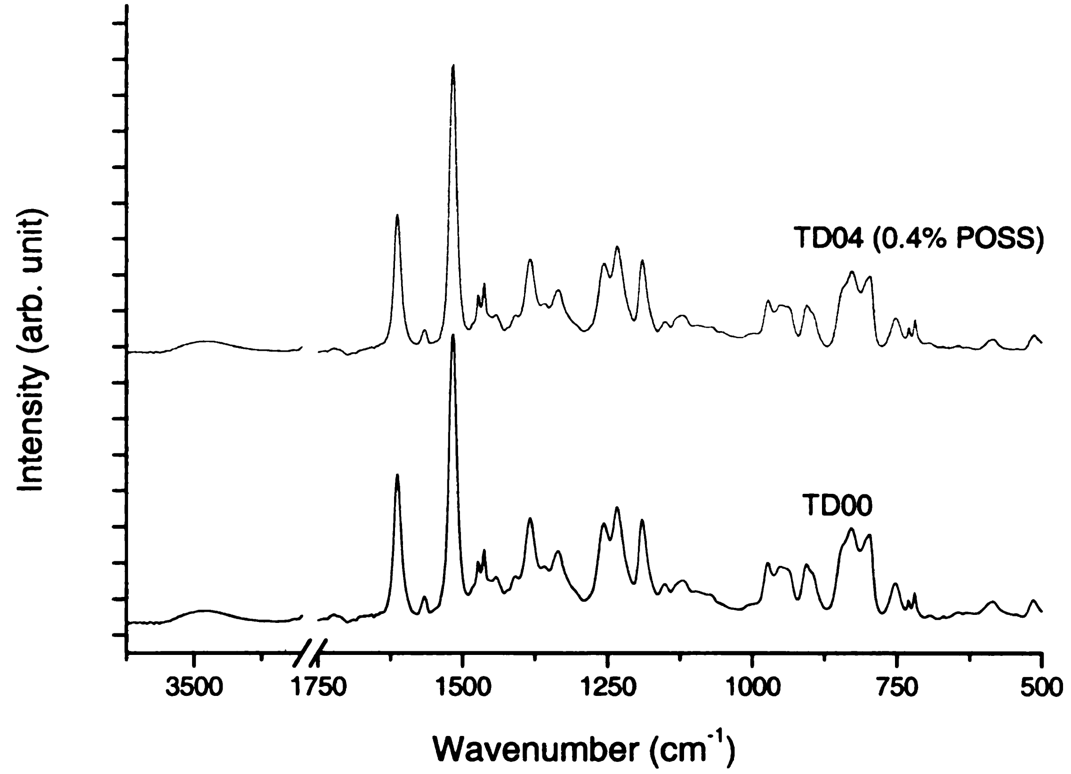
Figure 4-2 Epoxide consumption rate plotted against time for DGEBA-DytecA system



DD00= DGEBA / DytecA/0%trisilanol phenyl POSS; DD04= DGEBA/ DytecA / 0.4% trisilanol phenyl POSS known that the curing kinetics can be accelerated by strong acidic catalysts, such as BF_3, phenolic acid. Even though the acidity of trisilanol phenyl POSS could be close or superior to phenolic acid, the presence of POSS in the epoxy resin, however, did not revoke catalyzed reaction. To further quantitatively investigate this result, the conversion rate of epoxide was presented in Figure 4-2. The conversion of epoxide was calculated using the area of epoxide (914 cm^{-1}) at different curing time divided by the area of epoxide immediately after mixing the DGEBA and DytecA. As seen, the conversion of epoxide showed rapid increase in the first 15 mins. After that, the conversion of epoxide followed a decreased increasing rate. After 1020 min, the total conversion of epoxide was 28% in sample DGEBA/DYTECA/0% POSS and 22% in sample DGEBA/DYTECA/0.4% POSS. This conversion value is considerably low due to two facts: the curing temperature was 30°C lower than the T_g of the final product, and the DytecA actively reacted with DGEBA at room temperature initially during the process of mixing. Nevertheless, the calculation shows that the conversion of epoxide was lower for DGEBA/DYTECA/0.4% POSS in the total time frame, which supported our argument that the trisilanol phenyl POSS was not catalyzing the curing of epoxy resin. In a separate measurement, the conversion rate of epoxide showed no difference in DGEBA/DYTECA/0% POSS and DGEBA/DYTECA/0.4% POSS cured at 100°C (about 10°C higher than the Tg of the final product). Thus the slightly lower conversion rate in DGEBA/DYTECA/0.4% POSS is attributed to the increasing chain entanglements in the presence of POSS molecules at temperatures lower than Tg, where the epoxy network has much less mobility. This observation was in contrast to the filled silica system, where the curing kinetics was accelerated by a hypothesized free volume effect[22-23]. The researchers hypothesized that the presence of filled silica decreased the free volume of the system and thus increased the local concentration of epoxy monomers. In the epoxy-POSS system, however, we believe that the presence of nanosized POSS molecules did not significantly decrease the free volume. Furthermore, because the POSS molecules were much smaller than the conventional silica when dispersed at the molecular level, the interface between monomers and the POSS (the place where the catalysis effect is believed to take place) should be small. Thus, the filler effect, which hypothesized to cause high concentration of monomers at local area, should be minimum in this study.

The FTIR results on TGDDM based epoxy resin further supported the above argument. Two samples were subjected to the FTIR analysis: TGDDM/DYTECA/0%POSS and TGDDM/DYTECA/0.4%POSS. The curing temperature was 100°C (approximately 100°C lower than Tg) and 150°C. Figure 4-3 shows the FTIR results of these two samples after curing for 900 min at 100°C. As seen, there is no significant difference between these two samples. Quantitative calculation shows that sample TGDDM/DYTECA/0.4% POSS shows barely observable increase in hydroxyl peak at 3450 cm^{-1}. Similar observations were also found in samples cured at 150°C for 900 min.

Figure 4-1 FTIR results of TGDDM epoxy resin with DytecA



TD00= TGDDM / DytecA / 0% trisilanol phenyl POSS; TD04 = TGDDM / DytecA / 0.4% trisilanol phenyl POSS

CHAPTER 5

SUMMARY

The Glass transition temperature from the tanδ peak is used to characterize the cure state and its development during cure of an epoxy resin using trisilanol phenyl POSS as a promoter in the curing reaction. It is seen that there are significant increases in the glass transition temperatures for systems that are cured much below their glass transition temperatures.

Normally epoxides are cured with amines to improve specific properties or applications such as pot life, flexibility, speed of cure, lower toxicity, and lower exotherm in large castings. Though epoxies cured with aromatic amines form better cross linked systems than the aliphatic systems they require elevated temperatures to cure, also % amine reacted is very less compared to that of aliphatic amines.

In this study, we demonstrated that the addition of small quantities of trisilanol phenyl silsesquioxane (trisilanol phenyl POSS) molecules could induce a promoted network in epoxy resins. Dynamic Measurement Analysis (DMA) results showed that the trisilanol phenyl POSS containing POSS had a uniformly higher T_g than the neat epoxy amine system, only 0.2% trisilanol phenyl POSS showed a marked improvement in the glass transition temperature compared to the neat epoxy amine system and also this promotion of T_g was found to be independent of the POSS concentration. This suggests that the filler effects did not cause the increase in Tg. The increase in T_g was due to the acid

(tris

ami

epo

trisi

netv

reta

sec

to f

for

tem

acid catalyzed reaction by the acidic phenyl silanol groups present in the Silsesquioxane (trisilanol phenyl POSS).

It was postulated that phenyl silanols promoted the reaction of the secondary amine to form an improved network, since the later stage of the curing process between epoxy and amine is diffusion controlled, the size of POSS and the acidity of the phenyl trisilanol were the two main reasons for the epoxy amine system to form an improved network connectivity, even though the total mobility of the epoxy network might be retarded somewhat because of the presence of POSS molecules, the diffusion-controlled secondary amine reaction can still gain better local mobility around the POSS molecules to form a more balanced network. This observation is considered to have industry uses for ensuring better end use properties of the epoxy aliphatic amine systems at much lower temperature cures than their glass transition temperatures.

REFERENCES & NOTES

1. The pK_a of the cyclopentyl POSS trisilanol is reported to be 7.6. R. Duchateau, U. Cremer, R. J. Harmsen, S. I. Mohamud, H.C.L. Abbenhuis, R.A. van Santen, A. Messtsma, S. K. H. Thiele, M. F. H. van Tol, and M. Kranenburg, Organometallics 18,5447 (1999).
2. May, Clayton A. Epoxy resins: chemistry and technology, New York: M. Dekker, (1988)
3. O'Neil, L.A. and Cole C.P., J. Appl. Chem., 6:356 (1956)
4. Smith, I.T. Polymer 2:95 (1961)
5. Ingberman, A.K. and Walton, R.K. J.Polymer Sci, 28:468(1958)
6. Allen, F.J. and Hunter, W. M., J. Appl. Chem., 7:86(1957)
7. Goh, Y.; Iijima, T.; Tomoi, M, J. Polym. Sci., Polym. Chem., 40,2689 (2002)
8. Kim, W. G.; Yoon, H. G.; Lee, J. Y., J. Appl. Polym. Sci., 81,2711 (2001)
9. Baney, R.H., Itoh, M., Sakakibara A., and Suzuki, T. Chem. Rev. 95,1409(1995)
10. Lamela, C. P. et al., Analusis, 21(9), 367 (1993)
11. Henry Lee; Kris Neville, Epoxy Resins: their application and technology, McGraw-Hill Book Company, Inc (1957)
12. Lichtenhan, Joseph, D. Comments Inorg. Chem., 17(2), 115-130 (1995)
13. Feher, F. J. et al., Organometallics, 10,2526 (1991)
14. Feher, F. J. et al., J. Am. Chem. Soc., 116, 2145 (1994)
15. Feher, F. J. et al., J. Am. Chem. Soc., 113, 3618 (1991)
16. Miller, M. L., The Structure of Polymers, Reinhold Book Corporation, New York (1966)

17. a) T. Kakurai and T. Noguchi, J. Soc. Org. Syn. Chem. Jpn., 18, 485 (1960)*

17.b) T. Kakurai and T. Noguchi, Kogyo Kagaku Zasshi, 63, 294 (1960)*

17.c) T. Kakurai and T. Noguchi, Kogyo Kagaku Zasshi, 64, 398 (1961)*

17.d) T. Kakurai and T. Noguchi, Kogyo Kagaku Zasshi, 65, 827 (1962)*

18. S. Komori and T. Karaki, Kogyo Kagaku Zasshi, 62, 538 (1959)*

19. Y. Oshiro, T. Tsunoda, and S. Komori, Kogyo Kagaku Zasshi, 64, 2132 (1961)*

20. Y. Oshiro, M.Ochiai, and S. Komori, Kogyo Kagaku Zasshi, 64, 1588 (1961)*

21. J. F. Harrod, J. Polymer Sci., 1A, 385 (1963)

22. Paz-Abuin et al., J. Polym. Sci. Part A, 36, 1001 (1997)

23. Altmann, N.; Halley, P.J.; Cooper-White,J.; Lange, J., Macromol. Symp., 169,171 (2001)

* The references cited were not read but the content of which was translated and was referred by May, Clayton A. Epoxy resins: chemistry and technology, New York: M. Dekker, (1988)