CHARACTERIZATION AND CORROSION PERFORMANCE OF γ-GLYCIDOXYPROPYLTRIMETHOXYSILANE MODIFIED EPOXY POLYMER

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ABSTRACT

CHARACTERIZATION AND CORROSION PERFORMANCE OF γ-GLYCIDOXYPROPYLTRIMETHOXYSILANE MODIFIED EPOXY POLYMER

Epoxy polymers have been widely used in a protective coating and adhesive due to its strong adhesion, high chemical resistance, and good processing characterisitics. However; epoxy coatings absorbs moisture easily, and the diffusion of absorbed water into the epoxy–steel interface weakens the interfacial adhesion strength between epoxy and steel in corrosive enviroment, due to the presence of hydrophilic hydroxy group in the cured network (epoxy/amine reaction). In this study, commercial epoxy polymer was chemically modified by γ-glycidoxypropyltrimethoxysilane monomer under the catalysis organotin compound via the reaction between hydroxyl group in epoxy polymer and alkoxy group in silanes, aiming to enhance the corrosion performans of epoxy polymer. Commercial epoxy polymer and silane modifed epoxy polymer were characterized by NMR spectroscopy, FTIR spectroscopy, epoxy equivalent weight measurement, contact angle measurement, surface energy measurement, hardness test and MEK double-rub test. The results showed that γ-glycidoxypropyltrimethoxysilane has been successfully grafted to epoxy polymer. Corrosion performance was evaluated by salt spray test acording to ASTM B117. The results showed that the chemically modified epoxy coating perform an improvement in resistance againts the penetration of water in polymeric resin and beter protectiveness on metalic corrosion.

ÖZET

γ-GLİSİDOKSİPROPİLTRİMETOKSİ SİLAN İLE MODİFİYE EDİLMİŞ EPOKSİ POLİMERİN KARAKTERİZASYONU VE KOROZYON PERFORMANSI

Epoksi polimerler güçlü yapışma, yüksek kimyasal dayanıklılık ve kolay işlenebilirlik özellikleri nedeniyle koruyucu boya ve yapıştırıcı sektöründe geniş olarak kullanılmaktadır. Fakat epoksinin amin ile reaksiyonu sonucu oluşan epoksi kaplamada bulunan hidrofilik hidroksil grublarının etkisiyle, epoksi kaplama korozif ortamlarda nem çeker ve absorblanan nemin diffüzyonla epoksi-çelik arayüzeyine ulaşmasıyla yapışma kuvveti azaltır. Bu çalışmada epoksi polymerin korozyon performansını arttırmak amacıyla; ticari bir epoksi polimer kimyasal modifikasyona tabi tutuldu. Epoksi polimer ile γ-glisidoksipropiltrimethoksi silan monomer reaksiyonunda katalizör olarak organotin bileşik kullanıldı ve epoksi polimerde bulunan hidroksil grupların silan monomerin alkoksil gruplarıyla reaksiyona girmesi sağlandı. Ticari epoksi polimer ve modifiye epoksi polimerin karakterizasyonu için NMR spektrosopi, FTIR spektroskopi yöntemleri kullanıldı ve epoksi eşdeğer ağırlık, kontak açısı, yüzey enerjisi, sertlik ve MEK-dayanımı ölçüldü. Karakterizasyon sonuçları γ-glisidoksipropiltrimethoksi silanın ticari epoksi polimere başarıyla modifiye edildiğini göstermektedir. Ticari epoksi polimer ve modifiye epoksi polimerin korozyon performansı ASTM B117'ye uygun olarak tuz sisi yöntemi ile test edilmiştir. Test sonuçları kimyasal modifikasyon sonrasında epoksi kaplamanın nem difüzyonunun azaldığı ve korozyon dayanımının arttığı gözlendi.

To my mother Hamiyet Oturaklı;

and

To my nephews Arda Ersin & Doğaç Oturaklı;

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LIST OF ABBREVIATIONS

GPTMS	3-glycidoxypropyltrimethoxy
DTMS	Dodecyl-Trimethoxysilane
TEOS	Tetraethoxy Silane
VTES	Vinyltriethoxy Silane
MEK	Methyl Ethyl Ketone
DGEBA	Diglycidyl Ether of Bisphenol -A
BPA	Bisphenol A
ECH	Epichlorohydrin
MDA	Diaminodiphenylmethane
DBTL	Di-Butyl Tin Dilaurate
PE	Polyethylene
PP	Polypropylene
EEW	Epoxide Equivalent Weight
WPE	Weight Per Epoxide
Tg	Glass Transition Temperature
UV	Ultraviolet
PCB	Printed Circuit Board
ASTM	American Society for Testing and Materials
ISO	International Organization for Standardization
NMR	Nuclear Magnetic Resonance
FTIR	Fourier Transform Infrared Spectroscopy
ATR	Attenuated Total Reflectance
IR	Internal Reflection Element

CHAPTER 1

INTRODUCTION

Coating is a liquid, liquefiable, or mastic composition which after application to a substrate in a thin layer is converted to an opaque solid film that including mixtures of various materials. The questions arise as to how much of which materials, and how do these things relate. The materials fall into four general categories, as: resins, pigments, solvents and additives.

Coatings are often used as a protective layer over the metal substrate to prevent the substrate from the penetration of water and corrosive ion into the metal/coating interface in a manner deleterious to the function and appearance of an object. Epoxy coating was widely used a protective coating and adhesive due to its strong adhesion, high chemical resistance, and good processing characteristics. However; epoxy coating absorbs moisture easily, and the diffusion of absorbed water into the epoxy–steel interface weakens the interfacial adhesion strength between epoxy and steel, particularly in wet conditions due to the presence of hydrophilic hydroxyl group in the epoxy/amine cured network (Figure 1.1).

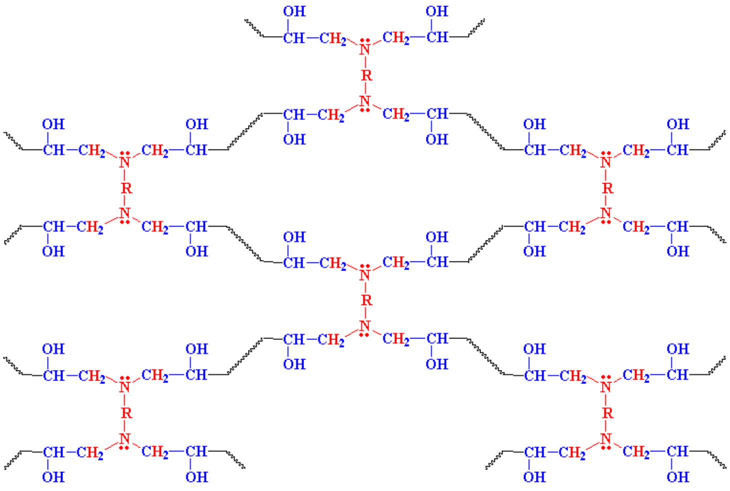


Figure 1.1. Epoxy / Amine Cured Net Work

(Source: PSLC, 2010)

To overcome epoxy hydrophilic properties drawbacks, silane have been used in,

- As additives for epoxy coatings (Simple mix)
- Chemical modification of epoxy polymer.

Silanes, hybrid organic-inorganic compounds, can function as mediators and promote adhesion between dissimilar, inorganic and organic, matrices through dual reactivity.

When silanes are used for as additives, they become a component of the coating from which they diffuse or migrate to inorganic substrate and react. Silanes, as additives, are generally effective in concentrations ranging from 0.05 to 1.00% of the coating (Plueddemann 1983). Nonetheless; effective coupling action with silanes as additives depends on meeting several criteria:

- Good mechanical dispersion of the silane into the coating will assure uniform coupling and best efficiency.
- The solubility parameters and reactivities of the polymer and silane must be compatible. No reaction should occur in storage. Matched solubility is necessary for silane interpenetration into the polymer (Chaudury 1987). Proper pH ranges must be maintained to avoid silane condensation.
- Silanes, as additives in filled systems, in storage will migrate to the inorganic surfaces of pigments and fillers. Some excess silane should be added for that which is adsorbed onto the mineral surface of the fillers and for the silane which fails to migrate through the polymer to the coating/substrate interface.
- Hydrolysis to silanetriol by water must occur to render the silane active for coupling. Proper moisture conditioning of filler or addition of extra water will help assure that the silane hydrolyzes and couples.

In the case of chemical modification of epoxy polymer, silane can be grafted to epoxy polymer via the reaction between hydroxyl group in epoxy resin and alkoxy group in silanes before their addition to the coating mixture (Figure 1.2). This is expected to reduce the drawbacks of silane usage as additives (Ji, et al. 2007).

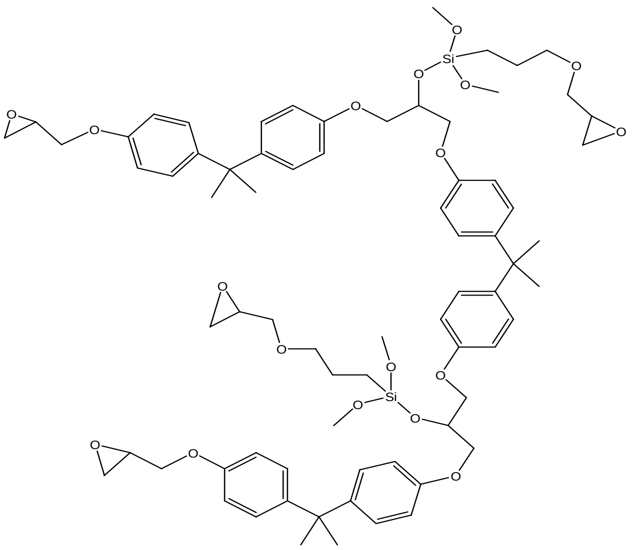


Figure 1.2. Silane Monomer Grafted to Epoxy Polymer

1.1. Literature Work

There are many studied related with silane and epoxy polymer in the literature. However most of the studies are on the using silane as additives for epoxy coatings (Ji, et al. 2006, Shon and Kwon 2006, van Ooij 2004, Plueddemann 1983).These studies reported good improvements in the epoxy polymer performances. Some of the studies on chemical modification of epoxy polymer by silane, on the other hand, will be summarized in the following paragraphs.

Ji et al., (2007) have been modified commercial epoxy resin chemically using different type of silane monomers ((1) Pure epoxy, (2) GPTMS, (3) DTMS, (4) TEOS, (5) VTES) under the catalysis of organotin compound, aiming to enhance the corrosion resistance of epoxy coating on 2024-T3 aluminum substrate (Figure 1.3).

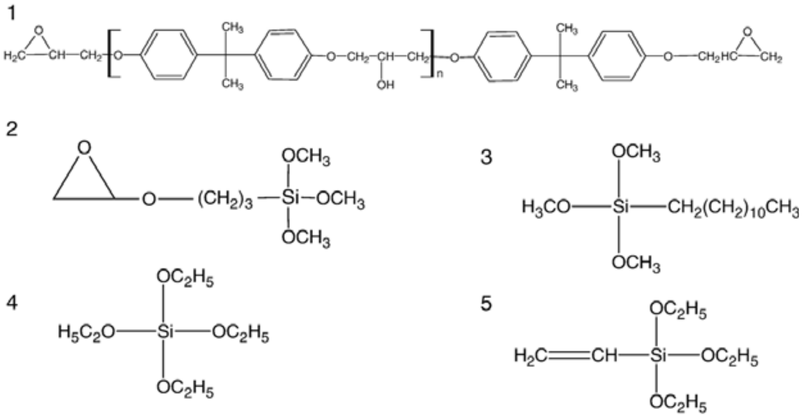


Figure 1.3. Chemically Modified Epoxy Resins with Various Silane Monomers (Source: Ji, et al. 2007)

In their synthesis process, epoxy resin, xylene and various silane monomers were mixed under the catalysis of organotin compound at 90 to 100 °C for 3 hours. The solvent (xylene) and the produce alcohol were removed under a reduced pressure and a viscous colorless product was obtained (Figure 1.4).

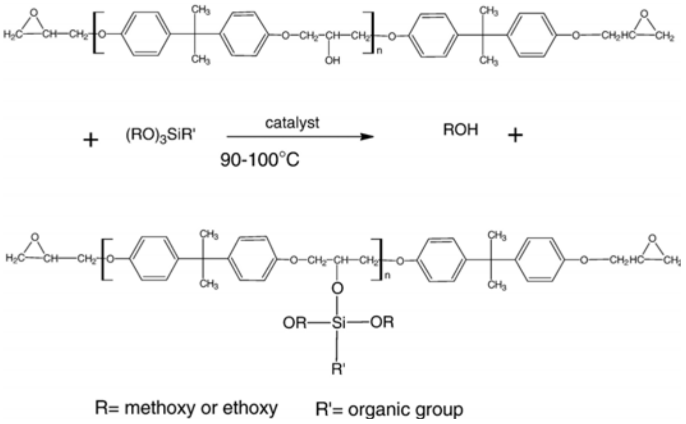


Figure 1.4. Synthesis Procedure of Modified Epoxy Resins with Various Silanes (Source: Ji, et al. 2007)

They concluded that, silane monomer could be successfully grafted to epoxy polymer according to FTIR results that showed a decrease in O–H stretching (3500 cm^{-1}) of the secondary hydroxyl in epoxy resin, an increase in peak intensity at 1000–1100 cm^{-1} increased obviously due to the formation of Si–O–C bonds. Additionally, they observed enhance the corrosion resistance of epoxy coatings on 2024-T3 aluminum substrates after silane modification.

In another study, Ji et al., (2006) have been modified epoxy polymer by γ-aminopropyltrimeyhoxysilane, aiming to enhance the corrosion resistance epoxy coating on aluminum alloys. In their synthesis process, epoxy resin, butanone and γ-aminopropyltrimeyhoxysilane were mixed 70 °C for 2 hours. The solvent was removed under a reduced pressure and a viscous colorless product was obtained (Figure 1.5).

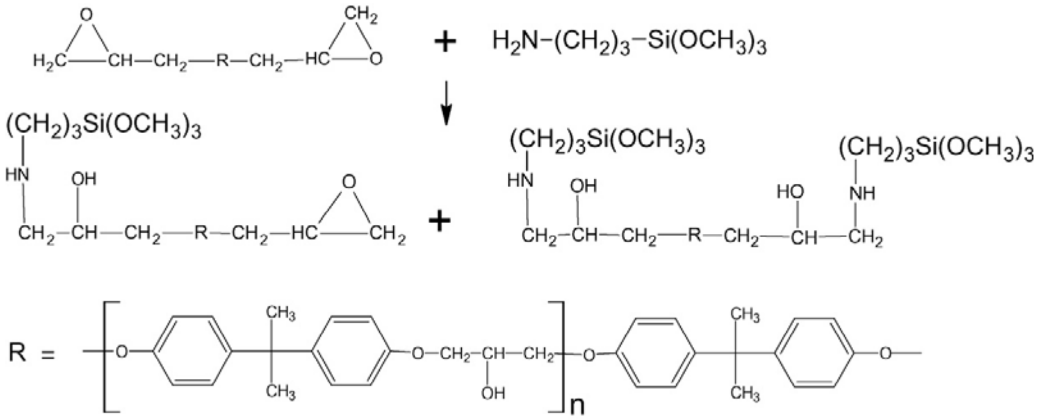


Figure 1.5. Synthesis Procedure of Modified Epoxy Resins with Amino Silane
(Source: Ji, et al. 2006)

In another study, Kahraman et al., (2006) have been studied the effect of organo alkoxy silane on the physical and mechanical properties of UV- curable epoxy acrylate protective coatings. For this purpose, they synthesized trimethoxysilane terminated HEPA urethane (TMSHU) oligomer to increase the compatibility between organic and inorganic network. In their synthesis process, trimethoxysilane modified HEPA urethane was prepared by the reaction of HEPA with 3-isocynato propyltriethoxysilane (Figure 1.6). Success of the reaction was confirmed by the disappearance of the characteristic –NCO peak at 2275 cm^{-1} in the FT-IR spectrum.

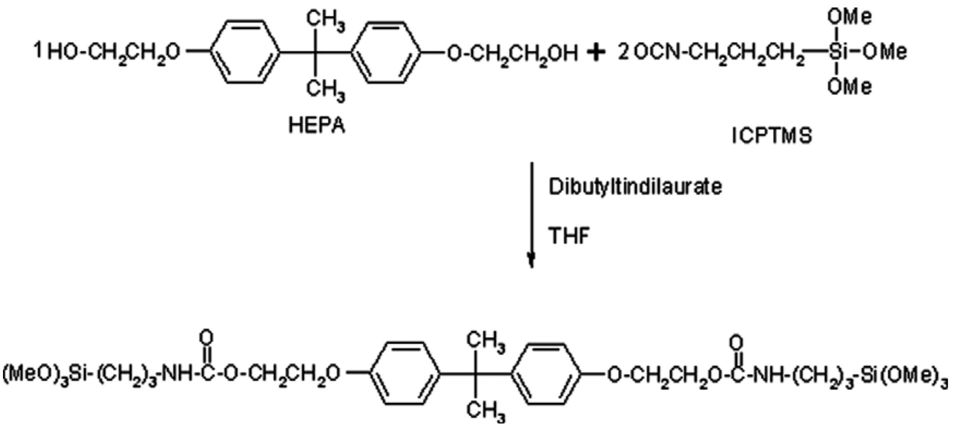


Figure 1.6. Synthesis Procedure of Trimethoxysilane Modified HEPA
(Source: Kahraman, et al. 2006)

As a result of this study, the pendulum hardness, cross-cut adhesion, gloss and impact strength of the coatings increased systematically with increasing methacryloxy propyltrimethoxysilane and trimethoxysilane terminated HEPA urethane content in the hybrid mixture.

In another study, Ahmad et al., (2005) have been studied the modification of diglycidyl ether of bisphenol A epoxy with hydroxyl-terminated poly dimethyl siloxane, through ring opening polymerization reaction. They evaluated thermal and corrosion performance of modified and unmodified polymers. In their study, epoxy polymer was preactivated at 120 ^{0}C for 30 minutes. The preactivated epoxy polymer and hydroxyl-terminated polydimethyl siloxane were mixed (Figure 1.7). The process was monitored by thin layer chromatography, by the determination of epoxy equivalent and hydroxyl value at regular intervals. In addition, the structure of siloxane-modified epoxy polymer was further confirmed by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectral analysis. As a result, they found siloxane-modified epoxy polymer to show better thermal and anticorrosive performance against to unmodified epoxy polymer.

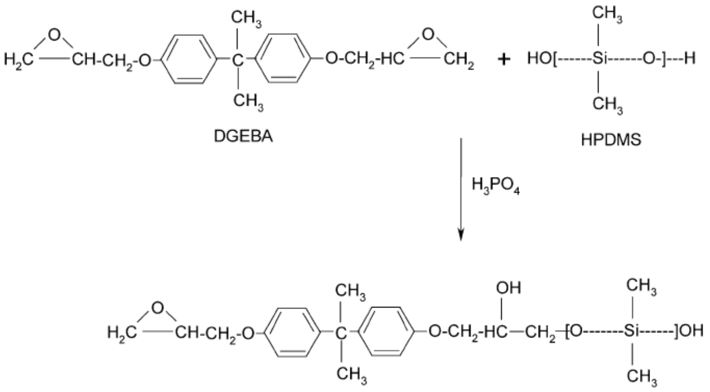


Figure 1.7. Synthesis Procedure of Polydimethyl Siloxane Modified Epoxy Resin (Source: Ahmad, et al. 2005)

In another study, Jiao et al., (2005), have been studied the vinyltrimethoxysilane and vinyltriethoxysilane grafted ethylene-octane copolymer in the melt process. They evaluated thermal stability and mechanical properties of silane modified and unmodified ethylene-octene copolymers. In this study, ethylene-octane copolymer pellets were premixed with vinyltrimethoxysilane (or vinyltriethoxysilane) and dicumyl peroxide. Their FTIR results suggested that silane have been successfully grafted onto ethylene-octene copolymers and both the thermal stability and the mechanical properties of silane modified ethylene-octene copolymers were better than unmodified ethylene-octene copolymers.

1.2. Aim of the Study

The aim of this study was to modify a commercial epoxy polymer by γ-glycidoxypropyltrimethoxysilane monomer under the catalysis organotin compound via the reaction between hydroxyl group in epoxy polymer and alkoxy group in silane aiming to enhance the corrosion performance of epoxy polymer. This work which focuses on detailed work and complete characterization is expected to complete the present works available in the literature to day.

γ-glycidoxypropyltrimethoxysilane is selected in this work due to (Figure 1.8) higher crosslink densities expected since γ-glycidoxypropyltrimethoxysilane has a epoxy functionality.

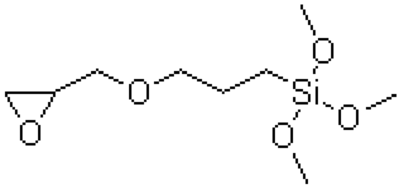


Figure 1.8. γ-glycidoxypropyltrimethoxysilane

A crosslink density is the average molecular weight or mass between crosslink points. A high crosslink density is considered to consist of multiblock chain with strong chemical crosslink (chemical junctions) and polar groups in the units introducing an additional polar interaction (physical junction) in the polymeric network in Figure 1.9 a) and b) (Shalin 1995). Increasing crosslink density improves coating's barrier properties against for penetration of water and corrosive ion into the metal / coating interface.

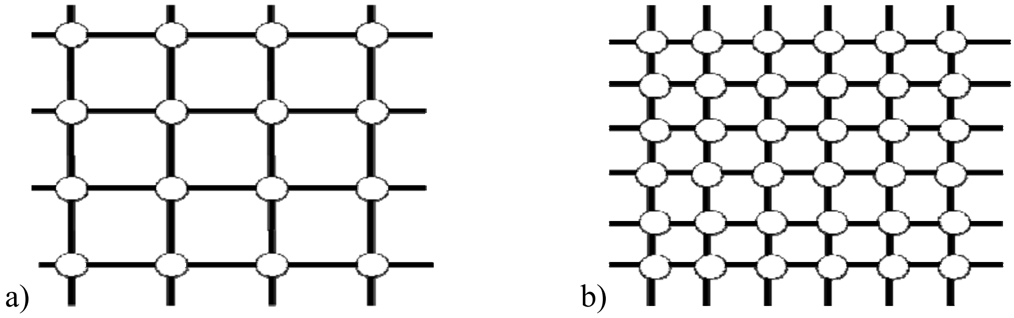


Figure 1.9. a) Low Crosslink Density b) High Crosslink Density

CHAPTER 2

EPOXY COATING

2.1. Coatings

In any civilized society, coatings are everywhere. There are coatings on the walls, refrigerator, cabinets, and furniture; less obviously, coatings are on the wires of electrical motors, printed circuits, inside television sets, and compact disks, car, as well as inside car, under the hood, and on components of the automotive stereo and computer systems.

Coatings can be described by their appearance (e.g. clear, pigmented, metallic, or glossy) and by their function (e.g. corrosion protective, abrasion protective, skid resistant, decorative or photosensitive). Coatings may be distinguished as organic or inorganic, although there is an overlap. For example, many coatings consist of inorganic pigment particles dispersed in an organic matrix (the binder). A confusing situation results from multiple meanings of the term coating. It is used to describe the material (usually, a liquid) that is applied to a substrate, the resulting “dry” film, and the process of application.

Coatings with organic binders that are applied purposefully to a substrate. Many types of coatings are not included. Porcelain enamels on kitchen ranges are coatings, but they do not have organic chemical binders. Electroplated copper, nickel, and zinc coatings are excluded for the same reason (Wicks 2007).

2.1.1. Composition of Coatings

Organic coatings are complex mixtures of chemical substances that can be grouped into four broad categories: (1) binders, (2) volatile components, (3) pigments, and (4) additives. Binders are the materials that form the continuous film that adheres to the substrate (the surface being coated), that bind together the other substances in the coating to form a film, and that present an adequately hard outer surface. In some cases, these polymers are prepared and incorporated into the coating before application; in other cases, final polymerization takes place after the coating has been applied. Binder polymers and their precursors are often called resins. The binder governs, to a large extent, the properties of the coating film.

Volatile components are included in a large majority of all coatings. They play a major role in the process of applying coatings; they are liquids that make the coating fluid enough for application, and they evaporate during and after application. Pigments are finely divided insoluble solid particles that are dispersed in the vehicle and remain suspended in the binder after film formation. Generally, the primary purpose of pigments is to provide color and opacity to the coating film. However, they also have substantial effects on application characteristics and on film properties. Although most coatings contain pigments, there are important types of coatings that contain little or no pigment, commonly called clear coats, or just clear. Clear coats for automobiles and transparent varnishes are examples. Additives are materials that are included in small quantities to modify some property of a coating. Examples are catalysts for polymerization reactions, stabilizers, and flow modifiers.

2.1.2. Methods of Film Formation

There are three general methods by which film-formers change from the liquid to the solid state:

1. Evaporation of the solvent.
2. Oxidation.
3. Polymerization.

Method 1 may be illustrated by the drying of shellac. A solution of shellac in alcohol, when applied in a thin layer, dries by simple evaporation of the alcohol, leaving a continuous film of shellac as the coating. The solvent may be allowed to evaporate from these coatings under normal room conditions, or evaporation may be accelerated by heating the coated object in an oven.

Method 2 may be illustrated by the drying of linseed oil. When linseed oil is spread as a thin film, it absorbs oxygen from the air, and changes from the liquid oil to the solid film of linoxyn. This method applies to drying oils, oleo resinous varnishes, oxidizing alkyd resins, and many other film forming materials. As a result of the oxidation of these materials, linkages are formed between two or more molecules, thereby producing a polymeric structure. The general process is referred to as autoxidative polymerization.

Method 3 is designated as polymerization, but we have seen that one type of polymerization occurs in method 2. There are two other general types, namely, condensation polymerization and addition polymerization. In this process a small molecule, usually water, is split off between two film-forming molecules, thereby producing a chemical bond between them. Addition polymerization occurs when unsaturated molecules, such as styrene or vinyl chloride, are activated by a suitable catalyst so that they add together to form large molecules.

The particular process which is used to form a film of coating material depends on the chemical composition of the film-former and on a characteristic usually referred to as its functionality. If a film-former has a functionality no greater than 2, it is capable of forming linear polymers only. If the film-former has a functionality of 3, it is capable of forming three-dimensional polymeric structures. The materials made up of linear polymers are known as thermoplastic, and also as non-convertible materials, since they soften when heat is applied, and remain soluble instead of being converted into insoluble materials. The materials consisting of three-dimensional polymeric structures are known as thermosetting, and also as convertible materials, since they do not soften appreciably when heated, and they become insoluble in the solvents from which they were applied (Payne 1954).

2.2. Corrosion Protection of Coatings

2.2.1. Corrosion

Corrosion is defined as the continuous destruction or deterioration of a material by chemical or electrochemical attack. The corrosion reaction is termed electrochemical as the overall corrosion reaction can be split in to two partial reactions. The anodic or oxidation reaction involves the metal going into dissolution by releasing electrons.

$$M \rightarrow M^{n+} + ne^{-} \tag{2.1}$$

Where M is the metal, M^{n+} is the metal oxidized to metal ions and ne- is the number of electrons produced during the anodic process.

The consumption of these electrons from the anodic reaction signifies a reduction or cathodic reaction. There are several cathodic reactions that occur in metallic corrosion, some common cathodic reactions are:

$$2H^+ + 2e^- \rightarrow H_2 \text{ (Hydrogen reduction reaction)} \tag{2.2}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \text{ (Oxygen reduction (acid solution))} \tag{2.3}$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \text{ (Oxygen reduction (basic and neutral))} \tag{2.4}$$

$$M^{3+} + e^- \rightarrow M^{2+} \text{ (Metal ion reduction)} \tag{2.5}$$

The hydrogen reduction reaction is seen when a metal is exposed to an acid medium, whereas the oxygen reduction reaction is most common in aqueous solutions which in contact with air are capable of producing this reaction. The metal ion reduction reaction is not frequently found in chemical media. The anodic and the cathodic reactions must occur simultaneously on the metal surface. The amount of electrons produced by the anodic reaction is consumed by the cathodic reaction and therefore charges neutrality is maintained.

2.2.2. Corrosion Control and Its Significance

The cost of corrosion control of metals in various industries exceeds over several billion dollars annually in the United States alone (Dickie 1986).Corrosion occurs in aircrafts, automobiles, pipelines and even household appliances. While corrosion is inevitable, the cost can be considerably reduced by protecting the metal surface. The important parameters to be considered in the corrosion process are the material that needs to be protected and the environment that it is exposed to. One can control corrosion process by either protecting the material or controlling the corrosiveness of the environment. As corrosion involves an anodic and a cathodic reaction, by controlling the rate of either reaction we can reduce the overall corrosion rate. Corrosion protection by organic or inorganic coatings has been successfully used to minimize the corrosion process for several years.

2.2.3. Corrosion Protection by Organic Coatings

Corrosion protection of metallic substrates has been one of the important roles performed by organic coatings. Such coatings remain cost-effective for many users who would like to have substrates coated just once and assume appearance and function will be maintained. Organic coatings are often used as a protective layer over the metal substrate to prevent the substrate from oxidizing in a manner deleterious to the function and appearance of an object. They do so in several ways (Bierwagen 1996). First, they act as a barrier limiting the passage of current necessary to connect the areas of anodic and cathodic activity on the substrate. This occurs especially if the coating wets the substrate surface very well and has good adhesion in the presence of water and electrolyte. Coatings do not really stop oxygen sufficiently to make concentrations at the surface rate limiting and they do not completely stop water ingress into coatings. However, a good barrier coating slows water and electrolyte penetrations and is not displaced by water at the substrate/coating interface (Bierwagen 1998).

The major areas where protective organic coatings are used are automotive coatings systems, appliance systems, metal coil coatings; powder coatings for heavy-duty use, especially pipeline coatings; farm and construction equipment coatings; and general use for objects used in exterior exposure. These are major Original Equipment Manufacturing areas where corrosion protection is critical. Industrial, architectural aircraft and marine equipments are other areas where coatings are important for the protection they offer against corrosion. Organic coatings are applied often as multi-layer systems called broadly as finishing system (Hess 1965). A full finishing system will require a metal pretreatment or conversion coating which is a special formulation of inorganic chemicals which react with the metal to produce a strongly adherent, corrosion-inhibiting conversion coating, such as a phosphate or chromate, on the metal surface. This coating often provides a better surface than the original metal oxide layer for obtaining good adhesion of the paint layers. Continuing on the requirements of a full finishing system, the next level of coating coated over a pretreatment is the primer system whose role is to enhance corrosion protection and provide adequate adhesion. A primer system also is a reservoir for pigments and inhibitors such as chromates and phosphates which leach out to protect cracks that develop when a coating undergoes weathering and damage (Sinko 2001). Epoxy resins, polyurethanes, alkyds, polysiloxanes, acrylates are some of the resins that are used as primers. On top of the primer system come the undercoat and the final finish systems. These are typically UV resistant paints such as polyesters, a final finish is provided to provide aesthetic appeal. All of these layers may not be used in a finishing system, the use or non-use of certain layers is dependent on factors such as size and shape of article, protection required, severity of exposure, cost of production etc. Figure 2.1 shows typical coating system.

TOP COAT (Appearance, protection against UV-lights)
MID COAT (Barrier protection effect, Inter coat adhesion)
PRIMER (Corrosion protection)
METAL SUBSTRATE

Figure 2.1. Typical Coating System

2.3. Epoxy Resin in Surface Coating

Epoxy resins are an important class of polymeric materials, characterized by the presence of more than one three-membered ring known as the epoxy, epoxide, oxirane, or ethoxyline group (Figure 2.2).

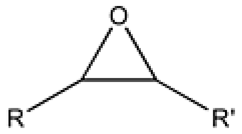


Figure 2.2. Three-Membered Ring
(Source: Wicks 2007)

The word “epoxy” is derived from the Greek prefix “ep,” which means over and between, and “oxy,” the combining form of oxygen. By strict definition, epoxy resins refer only to uncross-linked monomers or oligomers containing epoxy groups. However, in practice, the term epoxy resin is loosely used to include cured epoxy systems. It should be noted that very high molecular weight epoxy resins and cured epoxy resins contain very little or no epoxide groups. The vast majority of industrially important epoxy resins are bi- or multifunctional epoxides. The monofunctional epoxides are primarily used as reactive diluents, viscosity modifiers, or adhesion promoters, but they are included here because of their relevance in the field of epoxy polymers.

Epoxies are one of the most versatile classes of polymers with diverse applications such as metal can coatings, automotive primer, printed circuit boards, semiconductor encapsulants, adhesives, and aerospace composites. Most cured epoxy resins provide amorphous thermosets with excellent mechanical strength and toughness; outstanding chemical, moisture, and corrosion resistance; good thermal, adhesive, and electrical properties; no volatiles emission and low shrinkage upon cure; and dimensional stability—a unique combination of properties generally not found in any other plastic material. These superior performance characteristics, coupled with outstanding formulating versatility and reasonable costs, have gained epoxy resins wide acceptance as materials of choice for a multitude of bonding, structural, and protective coatings applications.

Commercial epoxy resins contain aliphatic, cycloaliphatic, or aromatic backbones and are available in a wide range of molecular weights from several hundreds to tens of thousands. The most widely used epoxies are the glycidyl ether derivatives of bisphenolA (>75%of resin sales volume). The capability of the highly strained epoxy ring to react with a wide variety of curing agents under diverse conditions and temperatures imparts additional versatility to the epoxies. The major industrial utility of epoxy resins is in thermosetting applications. Treatment with curing agents gives insoluble and intractable thermoset polymers. In order to facilitate processing and to modify cured resin properties, other constituents may be included in the compositions: fillers, solvents, diluents, plasticizers, catalysts, accelerators, and tougheners.

Epoxy resins were first offered commercially in the late 1940s and are now used in a number of industries, often in demanding applications where their performance attributes are needed and their modestly high prices are justified. However, aromatic epoxies find limited uses in exterior applications because of their poor ultraviolet (UV) light resistance. Highly cross-linked epoxy thermosets sometimes suffer from brittleness and are often modified with tougheners for improved impact resistance. The largest use of epoxy resins is in protective coatings (>50 %), with the remainder being in structural applications such as printed circuit board (PCB) laminates, semiconductor encapsulants, and structural composites; tooling, molding, and casting; flooring; and adhesives. New, growing applications include lithographic inks and photo resists for the electronics industry.

2.3.1. Classes of Epoxy Resins and Manufacturing Processes

Most commercially important epoxy resins are prepared by the coupling reaction of compounds containing at least two active hydrogen atoms with epichlorohydrin followed by dehydrohalogenation. These included polyphenolic compounds, mono and diamines, amino phenols, heterocyclic imides and amides, aliphatic diols and polyols, and dimeric fatty acids. Epoxy resins derived from epichlorohydrin are termed glycidyl-based resins. Alternatively, epoxy resins based on epoxidized aliphatic or cycloaliphatic dienes are produced by direct epoxidation of olefins by per acids.

Approximately 75% of the epoxy resins currently used worldwide is derived from DGEBA. This market dominance of bisphenol A based epoxy resins is a result of a combination of their relatively low cost and adequate-to superior performance in many applications.

2.3.2. Bisphenol A Epoxy Resins

The first epoxy resin used in coatings, and still by far the largest in volume, are bisphenol A (BPA) epoxies made by reaction BPA and ECH (Figure 2.3). Under basic condition the initial reaction is formation of BPA anion, which attacks ECH and Results in the formation of new oxirane ring with elimination of chloride anion.

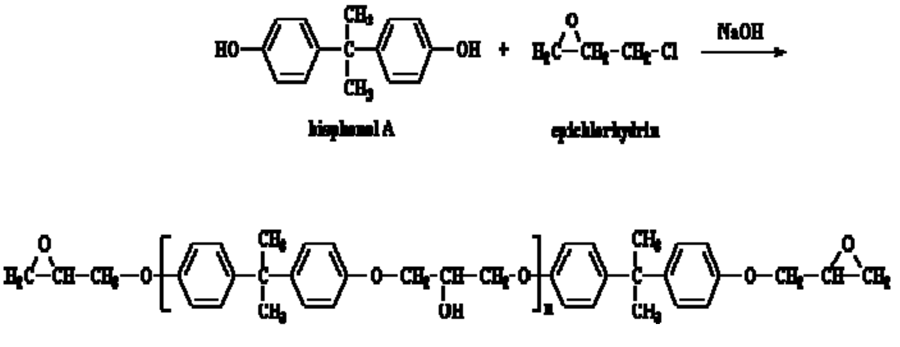


Figure 2.3. Diglycidyl Ether of Bisphenol-A (DGEBA) Epoxy Resin
(Source: Wicks 2007)

The molecular weight of the polymer is controlled by the ratio of ECH / BPA with a large excess of ECH, it is possible to make a resin that is dominantly DGEBPA, that is, where n=0 in the general formula. The pure n=0 compound is a crystalline solid but commercial grades of low molecular weight resin are liquid with n values of 0.11 to 0.15 (so called Standard liquid resin)

As the ratio of ECH/BPA is reduced, that is, as ECH/BPA approaches 1:1, the molecular weight and the n value of the epoxy resin increase. Viscosity also increases with molecular weight. Above an average n value of 1, the resin is largely amorphous solid. The commercially available higher molecular weight resins are often designated. Of course, as molecular weight increases, epoxy equivalent weight and average hydroxyl functionality also increase.

2.3.3. Curing of Epoxy Resin

In order to proceed from the relatively low molecular weight of the coating composition, as applied, to the high molecular weight polymer necessary for optimum film properties, a "curing" or polymerization must take place. The curing mechanisms are quite diverse and may involve either the epoxide or the hydroxyl groups on the resin molecule, or a combination of both (Fuller 1973).

Epoxy resins can be cured or cross linked by a large variety of chemical compounds. Namely, aliphatic and aromatic amines, acid anhydrides, and latent curing agents or catalysts. Other types of curing agents used in significant quantities in commercial applications are the phenols, carboxylic acids, ureas, inorganic acids and bases, and mercaptans. The high molecular weight epoxy resins are cured through the hydroxyl groups with phenols or ureas (Bruins 1968).

2.3.4. Amine- Epoxy Reaction

The chemical chosen to react with the epoxides is referred to as the curing agent (or hardener), and it typically has active hydrogen attached to nitrogen, oxygen, or sulfur. The selection of the curing agent depends on many parameters and will determine, to a large extent, the performance of the final epoxy thermoset. Amine curing agents are the most common and can be primary or secondary, aliphatic or aromatic, or cycloaliphatic. The amines typically have three reactive sites per molecule that facilitate the formation of a three-dimensional polymer network when mixed with the epoxy resin (Figure 2.4-Figure 2.7).

Amines electrons attack the carbon atoms next to the epoxide oxygen, giving a negative charge on the oxygen, and a positive charge on the nitrogen.

Figure 2.4. First Step of Amine- Epoxy Reaction
(Source: PSLC, 2010)

The oxygen's extra pair of electrons swipes hydrogen from the ammonium nitrogen for making an alcohol group and amine group.

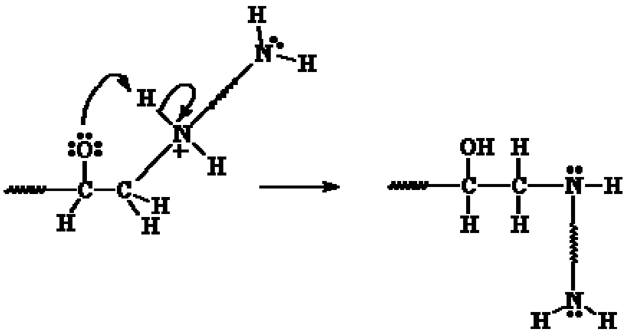


Figure 2.5. Second Step of Amine- Epoxy Reaction
(Source: PSLC, 2010)

Then two more epoxide group adds to the amine at other end of diamine.

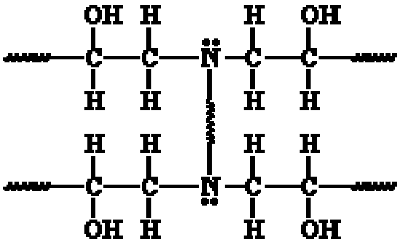


Figure 2.6. Third Step of Amine- Epoxy Reaction

(Source: PSLC, 2010)

In this manner, all the diamine molecules and all the diepoxy molecules become tied together in one big molecule.

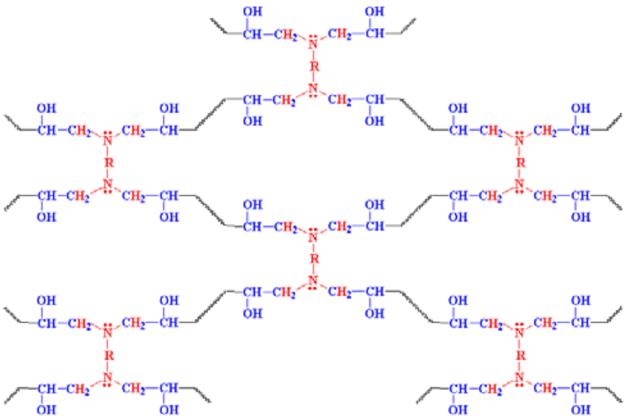


Figure 2.7. Last Step of Amine- Epoxy Reaction

(Source: PSLC, 2010)

Aliphatic polyamines such as diethylenetriamine, triethylenetetramine and other aliphatic hydrocarbon-based amines have been used for ambient-cure temperature epoxy resin systems in applications such as civil engineering, adhesives and architectural and maintenance coatings (Wegmann 1997). Unmodified polyamines tend to absorb moisture and carbon dioxide from the air, resulting in reduced coating performance. Cycloaliphatic such as isphoronediamine, bis-p-aminocyclohexylmethane and 1,2-diaminocyclohexane are used as epoxy resin curing agents for both ambient and heat-cure epoxy resin systems (Ghaemy 2004). While they have advantages as epoxy resin hardeners (light colors and good chemical resistance), they have the disadvantage of slow cure at low temperatures. Aromatic diamines such as diaminodiphenylmethane have been used as heat or ambient-curing hardeners after chemical modification.

In addition to the above types of curing agents there are also non-amine based curing agents. Either aromatic or aliphatic isocyanides may also be used as curing agents for epoxy resins. The isocyanides react through the hydroxyl groups of the epoxy resin and provide very good low temperature curing, good flexibility, good impact and abrasion resistance as well as good adhesion (Kieffer 2001). Epoxy resins contain secondary hydroxyl groups as reactive groups only or secondary hydroxyl plus amine. The isocyanides diffuses into the epoxy resin forming an interphase with a thickness of some micrometers. Depending on the functional groups available in the epoxy resin, urethane and urea groups are formed in the interphase (Kieffer 2001).

2.4. Properties of Silane

Silanes have been used as an adhesive agent in several applications (Plueddemann 1991). Silanes can be used to bind organic materials to inorganic substrates such as metals and glasses, silanes are used in a wide range of applications, performing a variety of functions including adhesion promotion and cross linking. They are used in paints, adhesives, inks, polishers, dyes, sealant primers etc. Silanes tend to improve the electrochemical and mechanical properties of the films they form (van Ooij 2004). Silanes are monomeric silicon compounds with four substituent groups attached to the silicon atom. These substituent groups can be nearly any combination of nonreactive, inorganically reactive, or organically reactive groups. They are represented generically as in Figure 2.8. Where R represents organofunctional groups, X_3 represents hydrolysable group and $(CH_2)_n$ alkyl chain acts as linker.

$$\mathbf{R\text{-}(CH_2)_n\text{-}Si\text{-}X_3}$$

Figure 2.8. Silane Structure

The general formula for a silane coupling agent typically shows the two classes of functionality. X is a hydrolyzable group typically alkoxy, acyloxy, halogen or amine. Following hydrolysis, a reactive silanol group is formed, which can condense with other silanol groups to form siloxane linkages. Stable condensation products are also formed with other oxides such as those of aluminum, zirconium, tin, titanium, and nickel. Alkali metal oxides and carbonates do not form stable bonds with Si-O-. The R group is a nonhydrolyzable organic radical that may possess a functionality that imparts desired characteristics.

2.4.1. Silane Application in Coatings

Silane has been used for improving performance of coatings. For example:

- Adhesion Promotor

Silanes can be formed chemical or physical bonds between the Adhesive/Sealant polymer structure and the inorganic or organic substrate (Figure 2.9).

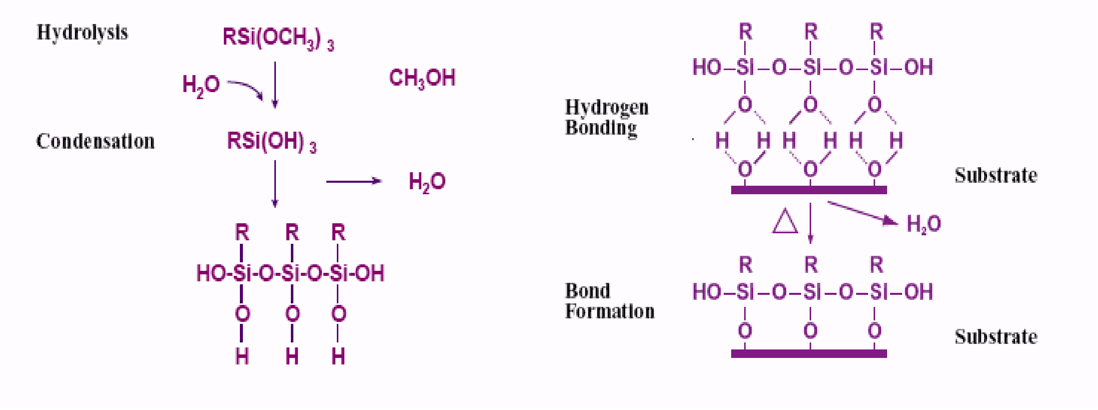


Figure 2.9. Mechanism of Silane Hydrolyses and Condenses
(Source: Evonik Industries, 2010)

- Cross linker

Silanes can be bonded to the polymer, the silane alkoxy groups are suitable for further chemical reaction (hydrolysis and condensation) (Figure 2.10).

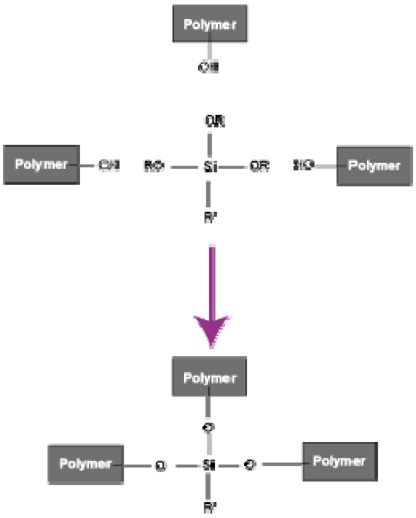


Figure 2.10. Crosslinker Mechanism
(Source: Evonik Industries, 2010)

- Pigment and Filler Modification

The hydrophilic surface most mineral fillers and pigments can be made hydrophobic to be more compatible with hydrophobic polymer (Figure 2.11).

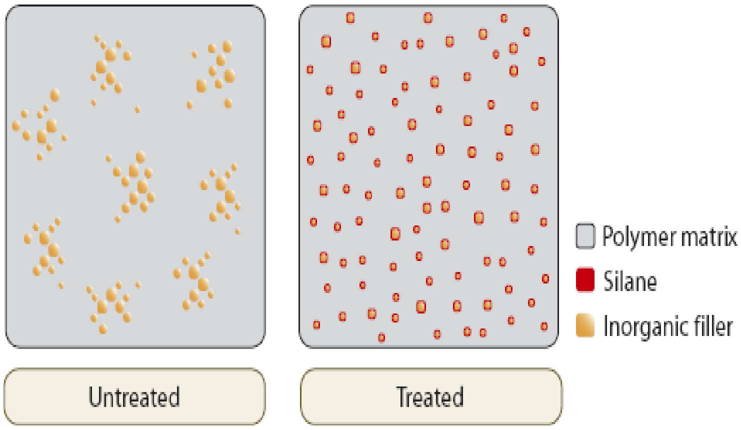


Figure 2.11. Pigment&Filler Modification
(Source: Evonik Industries, 2010)

- Co monomer

Silanes can be used as a monomer for improving the polymer performance (Figure 2.12).

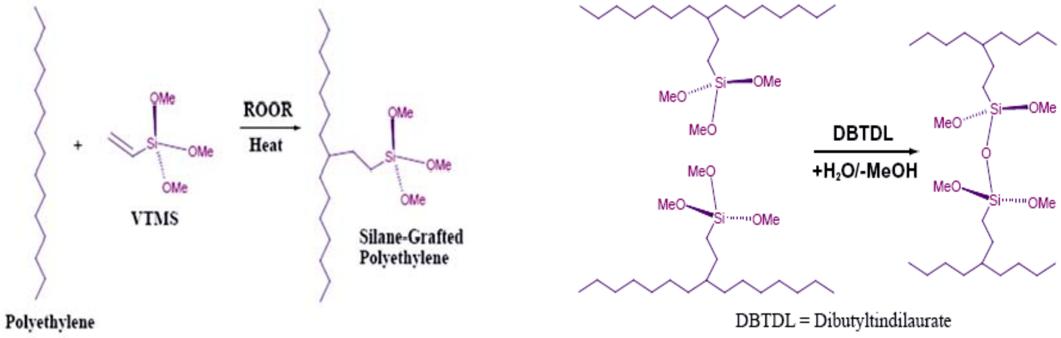


Figure 2.12. Silane as a Co monomer
(Source: Evonik Industries, 2010)

- Sol Gel Coating in Figure 2.13.

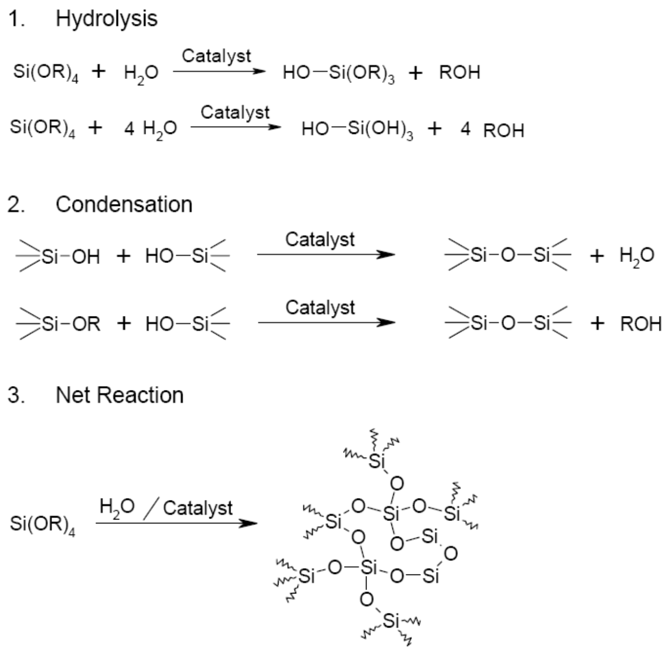


Figure 2.13. Sol Gel Coating
(Source: Evonik Industries, 2010)

CHAPTER 3

EXPERIMENTAL WORK

3.1. Raw Materials

3.1.1. Razeen SL 4175X75 Solid Epoxy Resin

It was commercially available from Jana and had an E.E.W. of 600-670 and repeating unit (N) of 2 (Figure 3.1).

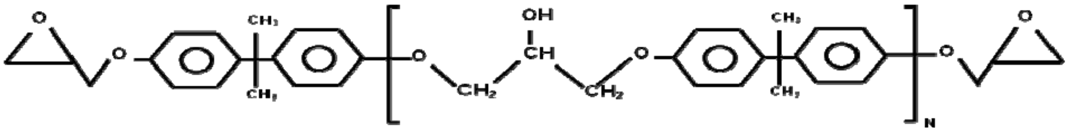


Figure 3.1. Epoxy Resin
(Source: Wicks 2007)

3.1.2. γ-glycidoxypropyltrimethoxysilane Monomer

It was commercially available from Dow Corning and had a molecular weight of 236, 34 g/mol (Figure 3.2).

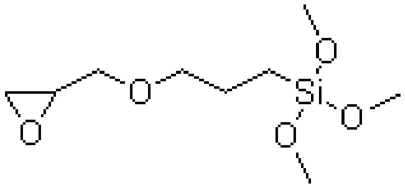


Figure 3.2. γ-glycidoxypropyltrimethoxysilane

3.1.3. Organotin Catalyst

Di-butyl tin dilaurate (DBTDL) catalyst having the Formula $C_{32}H_{64}O_4Sn$ was used. This tin catalyst is commercially available from Goldschmidt (Figure 3.3).

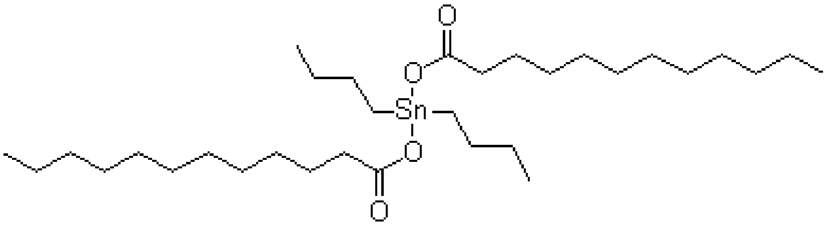


Figure 3.3. Di-Butyl Tin Dilaurate

3.2. Synthesis of γ-glycidoxypropyltrimethoxysilane Modified Epoxy

780 g epoxy resin and 129 g xylene were added into a 2000 ml four-necked flask, equipped with a mechanical stirrer, a reflux condenser and heated up to 140 ^{0}C (Figure 3.4). When it reaches to 140 ^{0}C, 388 g of γ-glycidoxypropyltrimethoxysilane and certain amount of organotin compound respectively were added a balance. This addition took three hours. The solvent (xylene) and the produce alcohol were removed under vacuum and a viscous colorless product was obtained.

Figure 3.4. Synthesis Equipment

3.3. Characterization Techniques

3.3.1. NMR analysis

The NMR Spectrum serves as a great resource in determining the structure of an organic compound by revealing the hydrogen and carbon skeleton. Historically, NMR was initially used to study the nuclei of Hydrogen atoms; however, any atom with an odd mass or atomic number has a nuclear spin that can be studied by NMR. Without the application of an applied magnetic field, protons are spinning in a randomly oriented manner and are generating a magnetic field (called the magnetic moment). However, once an external (applied) magnetic field is present the protons either align with (parallel) or against (anti parallel) it. The parallel orientation, called the alpha spin, has a lower energy than the anti parallel (beta) spin. The stronger the applied magnetic field the greater the energy difference (ΔE) between the parallel and anti parallel states (Figure 3.5). Therefore, the strength of the magnetic field determines the energy required to cause a nuclear spin flip. The energy difference (ΔE) between the ground and excited states is approximately 0.02 cal/mol which correlates to radio wave photons. An NMR signal is created once the radio wave photons supplied match the (ΔE) of the nucleus.

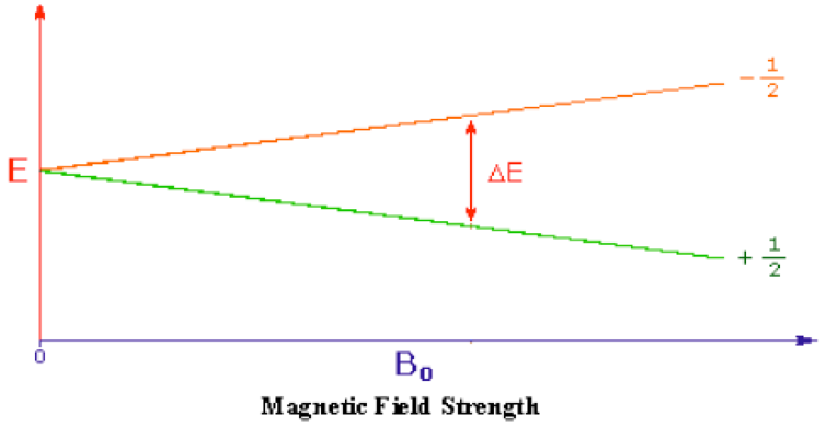


Figure 3.5. (ΔE) Between the Parallel and Anti Parallel States
(Source: UCLA, 2010)

NMR is used for to identify and/or elucidate detailed structural information about chemical compounds. For example:

- Determining the purity of medicines before they leave the factory
- Identifying contaminants in food, cosmetics, or medications
- Helping research chemists discover whether a chemical reaction has occurred at the correct site on a molecule
- Identifying drugs seized by police and customs agents
- Checking the structure of plastics or polymer, to ensure they will have the desired properties

3.3.2. FT-IR Spectroscopy Attenuated Total Reflectance (ATR)

Spectroscopy is the study of the interaction of electromagnetic radiation with a chemical substance. The nature of the interaction depends upon the properties of the substance. When radiation passes through a sample (solid, liquid or gas), certain frequencies of the radiation are absorbed by the molecules of the substance leading to the molecular vibrations. The frequencies of absorbed radiation are unique for each molecule which provides the characteristics of a substance. The electromagnetic spectrum covers an immense range of wavelengths. Table 3.1 a shows schematic of interaction of radiation with matter. The infrared regions are classified as follows:

Table 3.1. Schematic of Interaction of Radiation with Matter

Region	**Wavelength Range, µm**	**Wavenumber, cm^{-1}**
Near (NIR)	0.78 – 2.5	12,800 – 4,000
Middle (MIR)	2.5 – 50	4,000 – 200
Far (FIR)	50 – 1000	200 – 10

The principle of ATR-IR spectroscopy is illustrated in Figure 3.6. For multiple internal reflection and for thin deposited film. In contrast to transmission IR (T-FTIR) spectroscopy where the IR beams passes directly through the sample in the ATR mode and IR radiation is reflecting through the internal reflection element (IRE) and IR transparent crystal of high refractive index in contact with the sample. The IR radiation propagates through the IRE at an angle of incidence larger than the critical angle, such that total reflection occurs at the IRE-sample interface. An evanescent electromagnetic field is generated that penetrates into the sample and is attenuated by the sample, thus producing an IR spectrum.

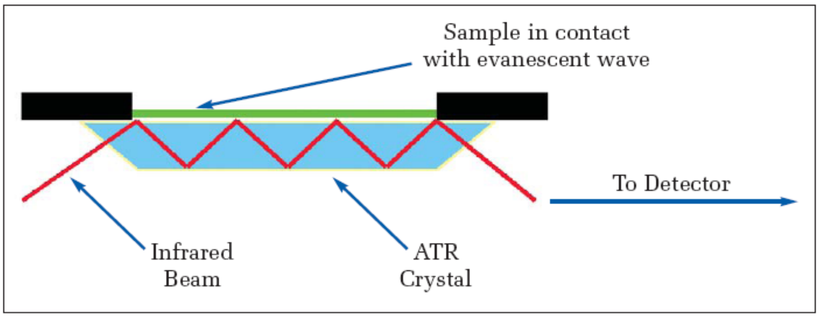


Figure 3.6. The Principle of ATR-IR Spectroscopy
(Source: PerkinElmer, 2010)

3.3.3. Epoxide Equivalent Weight.

The epoxy content of liquid resins is frequently expressed as epoxide equivalent weight (EEW) or weight per epoxide (WPE), which is defined as the weight in grams that contains 1 g equivalent of epoxide. A common chemical method of analysis for epoxy content of liquid resins and solid resins is titration of the epoxide ring by hydrogen bromide in acetic acid. Direct titration to a crystal violet indicator end point gives excellent results with glycidyl ethers and cycloaliphatic epoxy resins. The epoxy content of glycidyl amines is determined by differential titration with perchloric acid. The amine content is first determined with perchloric acid. Addition of tetrabutylammonium iodide and additional perchloric acid generates hydrogen iodide, which reacts with the epoxy ring. The epoxy content is obtained by the second perchloric acid titration to a crystal violet end point. In another procedure, a halogen acid is generated by the reaction of an ionic halide salt, e.g., tetraethylammonium bromide in acetic acid with perchloric acid with subsequent formation of a halohydrin; the epoxy group is determined by back-titration with perchloric acid using crystal violet indicator (Ording 1996). The end point can be determined visually or potentiometrically. This is the method adopted by ASTM and is currently used by most resin producers.

3.3.4. Preparation of Coating

Coatings were prepared with epoxy polymer and γ-glycidoxypropyltrimethoxy silane modified epoxy polymer. Coating formulation was given in Table 3.2.

Table 3.2. Coating Formulation

Ingredient	Amount
Polymer	% 60
Butyl glycol	% 1,3
Tego Dispers 670	% 0.5
Tipure R 902	% 30
Tego Airex 980	% 0.2
Isobutanol	% 4
n-Butyl Acetate	% 4

3.3.5. Preparation of Test Panel

60 µm dry film thickness was applied on metal test panels by Sheen 4500 in Figure 3.7. Then, the test panels were cured in room temperature for seven days.

Figure 3.7. Sheen 4500

3.3.6. Film Thickness Measurement

An Elcometer Thickness Gauge was used to measure the thickness of coating on metal plates.

3.3.7. MEK double-rub test

The MEK solvent-rub test is a well-known and frequently used test throughout the coatings industry. Its primary utility is to determine the extent to which a coating is cured and when interpreted properly, can be a very useful tool. The test itself is simple; a cotton ball or rag is soaked in MEK and rubbed over the surface of the coating a given number of times (Figure 3.8). The effect on the surface is then evaluated in terms of gloss loss, softening, or degree of rub off. The results of this type of test provide a measure of the chemical resistance of a given coating. When the results are compared to those of a control, known to be fully cured, a good qualitative determination of the degree of cure can be made.

Figure 3.8. MEK Double-Rub Tester

3.3.8. Pendulum Hardness Test

A Braive-Instruments Persoz Pendulum, (Model: 3034), was used (Figure 3.9). The coated glass plate was placed in hardness instrument and test was applied. Hardness of coating was measured from the number of oscillations of the pendulum swinging on the test panel. While the hardness of resin increased, the number of oscillations increased because the increase of hardness of a film decreased the effect of friction. The test was carried out in accordance with the ASTM D4366 standard.

Figure 3.9. A Braive-Instruments Persoz Pendulum

3.3.9. Contact Angle Measurements

One way to quantify a liquid's surface wetting characteristics on a coating surface is to measure the contact angle of a drop of liquid placed on the coating surface. The contact angle is the angle formed by the coating/liquid interface and the liquid/vapor interface measured from the side of the liquid. Wetting ability of a liquid is a function of the surface energies of the solid-gas interface, the liquid-gas interface, and the solid liquid interface. The surface energy across an interface or the surface tension at the interface is a measure of the energy required to form a unit area of new surface at the interface. The intermolecular bonds or cohesive forces between the molecules of a liquid cause surface tension. When the liquid encounters another substance, there is usually an attraction between the two materials. The adhesive forces between the liquid and the second substance will compete against the cohesive forces of the liquid. Liquids with weak cohesive bonds and a strong attraction to another material (or the desire to create adhesive bonds) will tend to spread over the second material. Liquids with strong cohesive bonds and weaker adhesive forces will tend to bead-up or form a droplet when in contact with the second material. To determine the hydrophobic or hydrophilic nature of the coated surface deionized water droplet coming out of a syringe was used to wet the coating surface. The contact angle obtained was used in comparative analysis and the coating surface was thus characterized. Higher contact angles indicate higher hydrophobicity of the coating.

3.3.10. Surface Energy Measurements

A solid is defined as materials that rigid and resists stress. A solid surface may be characterized by its surface free energy and surface energy. Surface tension is normally measured in energy units called dynes (mN). A dyne is the amount of force required to produce an acceleration of 1cm/sec on a mass of 1g. The dyne level of a material is called its surface energy. DYNE TEST marker pens can be used to measure the surface energy of films and other non-absorptive substrates. This method parallels ASTM Std. D2578, which covers the testing of polyethylene (PE) and polypropylene (PP) films via the application of formamide/ethyl Cellosolve solutions. The fluids used in DYNE TEST marker pens are based on those specified in ASTM D2578; the critical difference between this test and the ASTM technique is the manner in which the fluids are applied to the test sample.

3.3.11. Dyne Level Measurement

Application of DYNE TEST marker pens is; Draw a line across the material being tested. Apply sufficient vertical pressure to enable a good ink flow. Excessive pressure will adversely affect film surface treatment levels.

- **Properly Treated:**

The ink lies evenly on the material in a continuous line. There is no ink reticulation. The surface tension of the material is at, or higher than, the dyne level of the ink (Figure 3.10).

- **Not Treated:**

The ink reticulates into droplets. The surface tension of the material is well below the dyne level of the ink (Figure 3.10).

- **Partial Treatment:**

The ink line is defined but there is partial reticulation from the edges. The surface tension of the material is just below the dyne level of the ink (Figure 3.10).

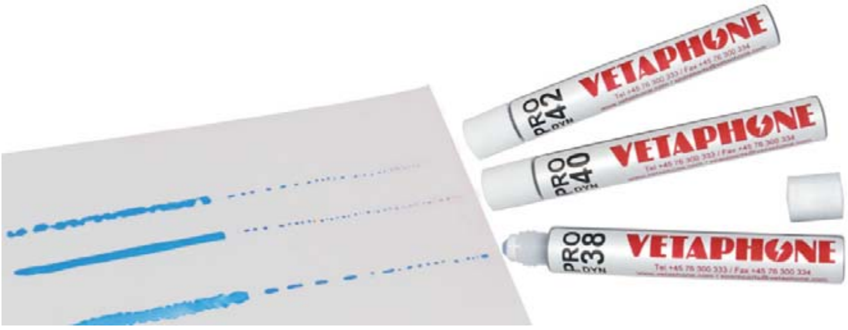


Figure 3.10. Dyne Level Measurement
(Source: Vetaphone, 2010)

3.3.12. Corrosion Performance.

The ASTM B117 salt spray test is the most widely used cabinet test to evaluate the corrosion performance of organic coatings in an accelerated corrosive environment. The coatings to be tested are prepared and suspended in a sealed chamber where they are subjected to a spray or fog of a neutral 5% salt solution which is atomized at a temperature of 37° C. The corrosive fog creates a 100 % relative humidity conditions in the chamber. The exposure time of the test specimen may vary from a few hours to several thousand hours, depending upon the type of the coating and its thickness. ASTM B117 states that the test is useful for providing relative corrosion resistance information for specimens in a given test chamber, but that the prediction of performance in natural environments has seldom been correlated with salt spray results. The standard further adds that the amount of corrosion seen is highly dependent on the type of materials tested and the control of the operating variables (e.g., atomization, salinity, temperature). In this study, these tests were performed in the salt spray chamber at Kanat Paints and Coating Company. Specimens were placed in a salt fog chamber according to ASTMB117 (Figure 3.11).

Figure 3.11. Salt Spray Chamber

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Characterization of Modified Epoxy

4.1.1. NMR Analysis

Chemical structure of epoxy polymer samples was analyzed by ^{1}H-NMR and ^{13}C-NMR spectroscopy. ^{1}H-NMR spectrum of epoxy polymer shown in Figure 4.1 depicts characteristic peaks of epoxy structure as shown in molecular formula. Since the polymer sample was dissolved in meta- and orto-xylene, peaks of H atoms that belonged to xylene were also observed. An unexpected peak that was determined as aliphatic –CH_2- was also observed. This peak might have been originated from possible impurities in either polymer or solvent.

Figure 4.2 shows ^{1}H-NMR spectrum of silane modified epoxy polymer. Specific peaks xylene was observed again. Methyl groups of silane are distinct from that of epoxy since they were attached to O atom next to Si and could be easily distinguished.

^{13}C-NMR analysis of pure epoxy polymer and silane modified epoxy polymer are consistent with H-NMR results (Figure 4.3 and Figure 4.4). Characteristic peaks of the specific C atoms of the related structures were labeled as in unattached silane was eliminated under vacuum prior to NMR analysis.

Analysis of both H and C atoms of the polymer samples were achieved by CS chemdraw 8.0. H-NMR and C-NMR spectrums of analyzed samples were compared to estimated structural analysis of the molecules. Estimated NMR spectrums are given in Appendix A.

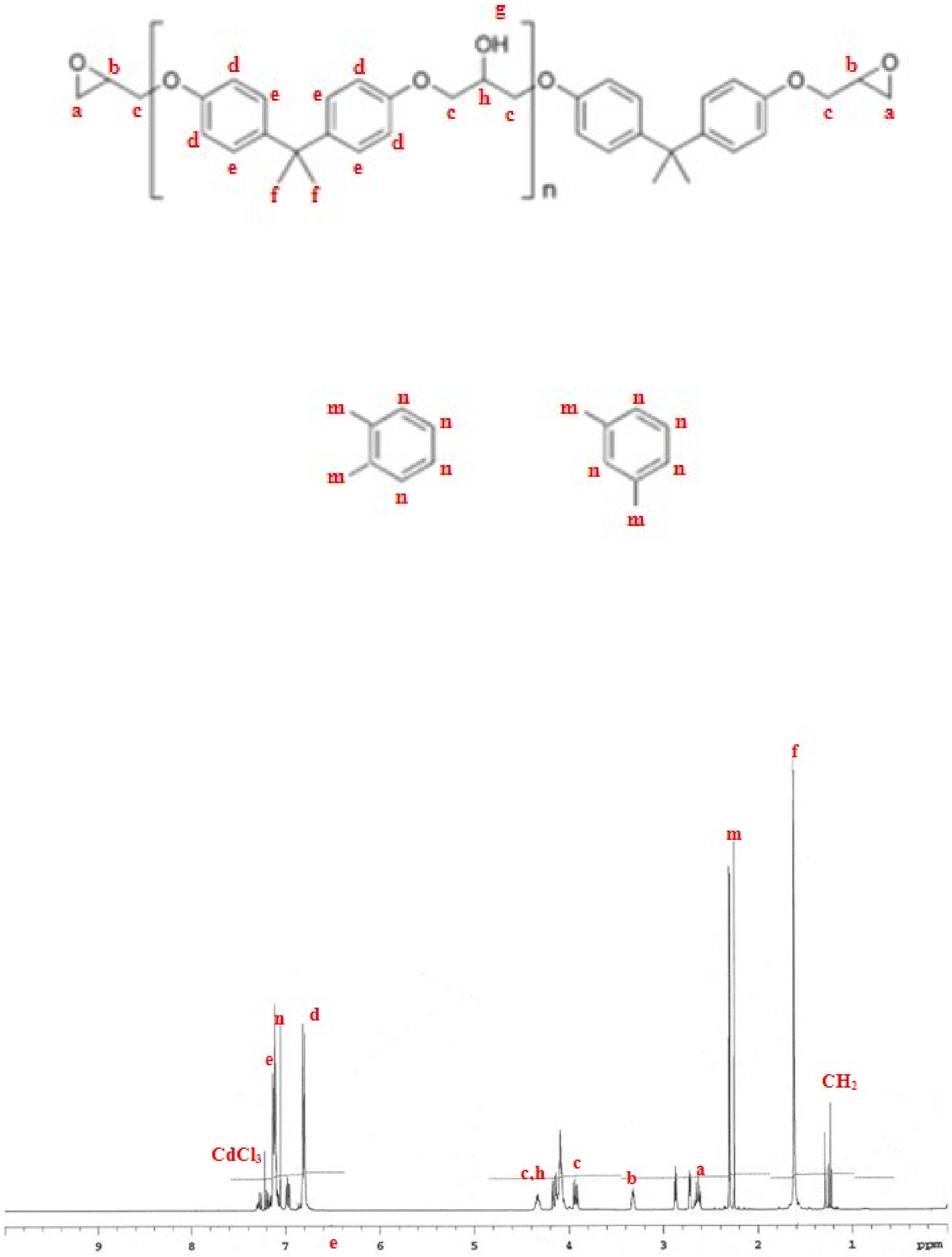


Figure 4.1. ^{1}H-NMR of Pure Epoxy

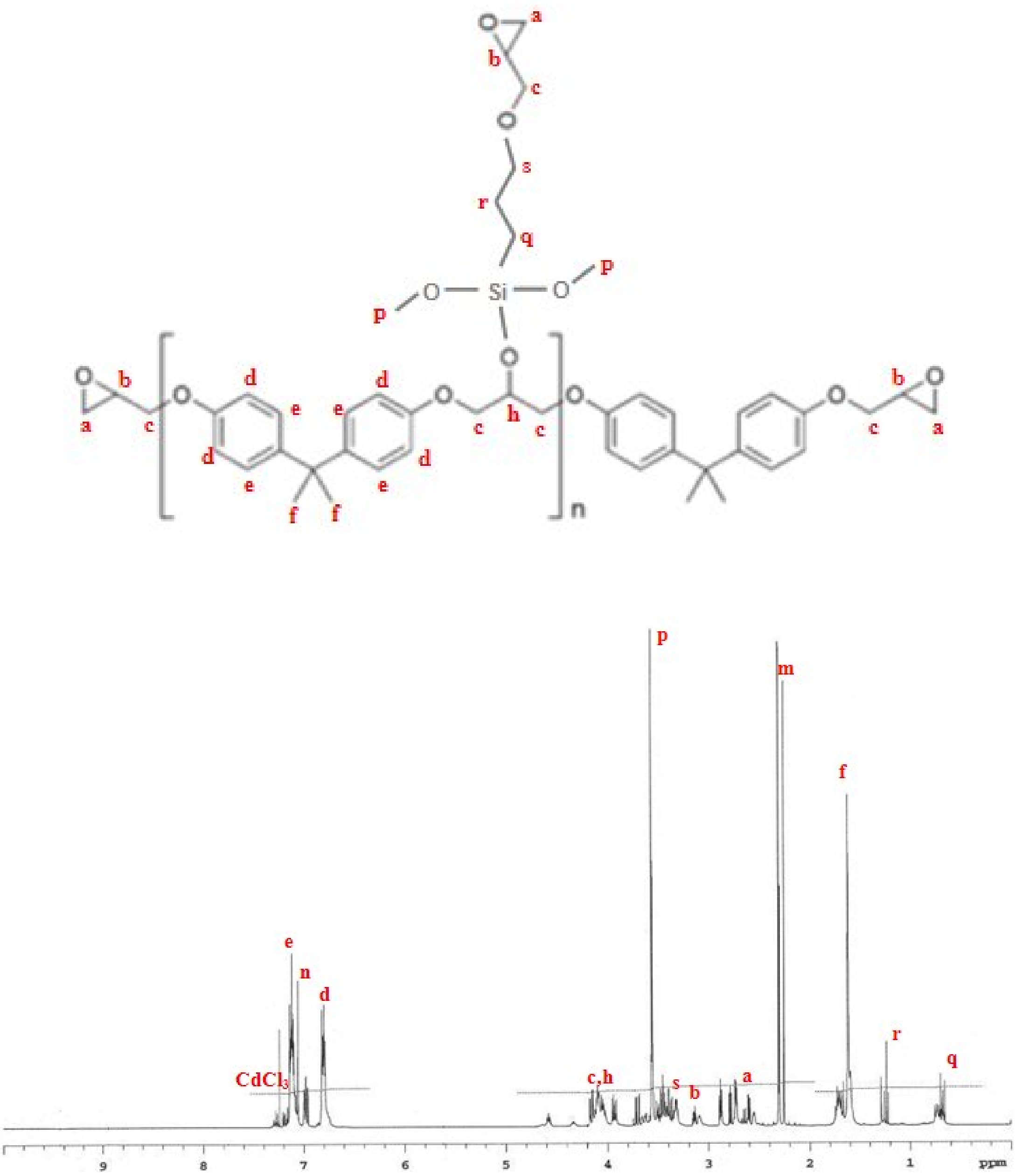
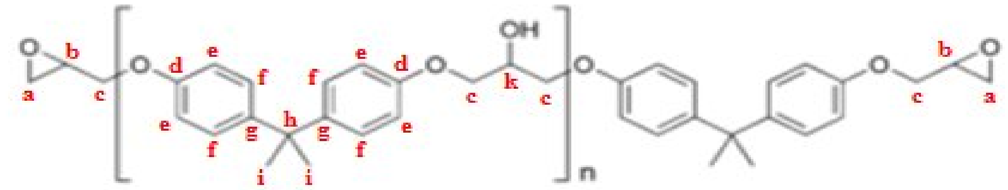
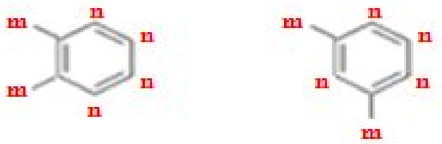


Figure 4.2. ^{1}H-NMR of Modified Epoxy





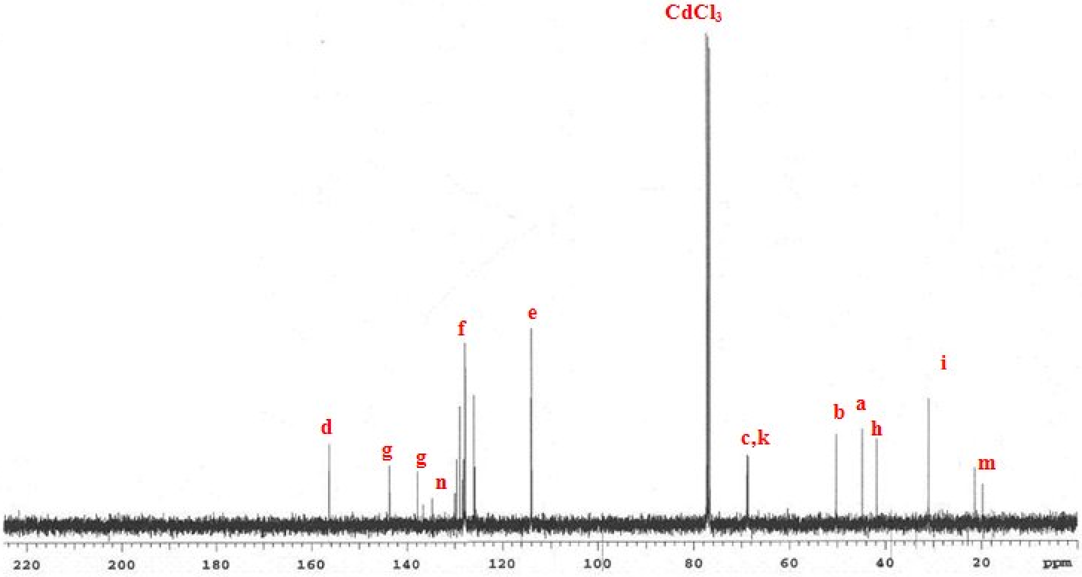


Figure 4.3. ^{13}C-NMR of Epoxy

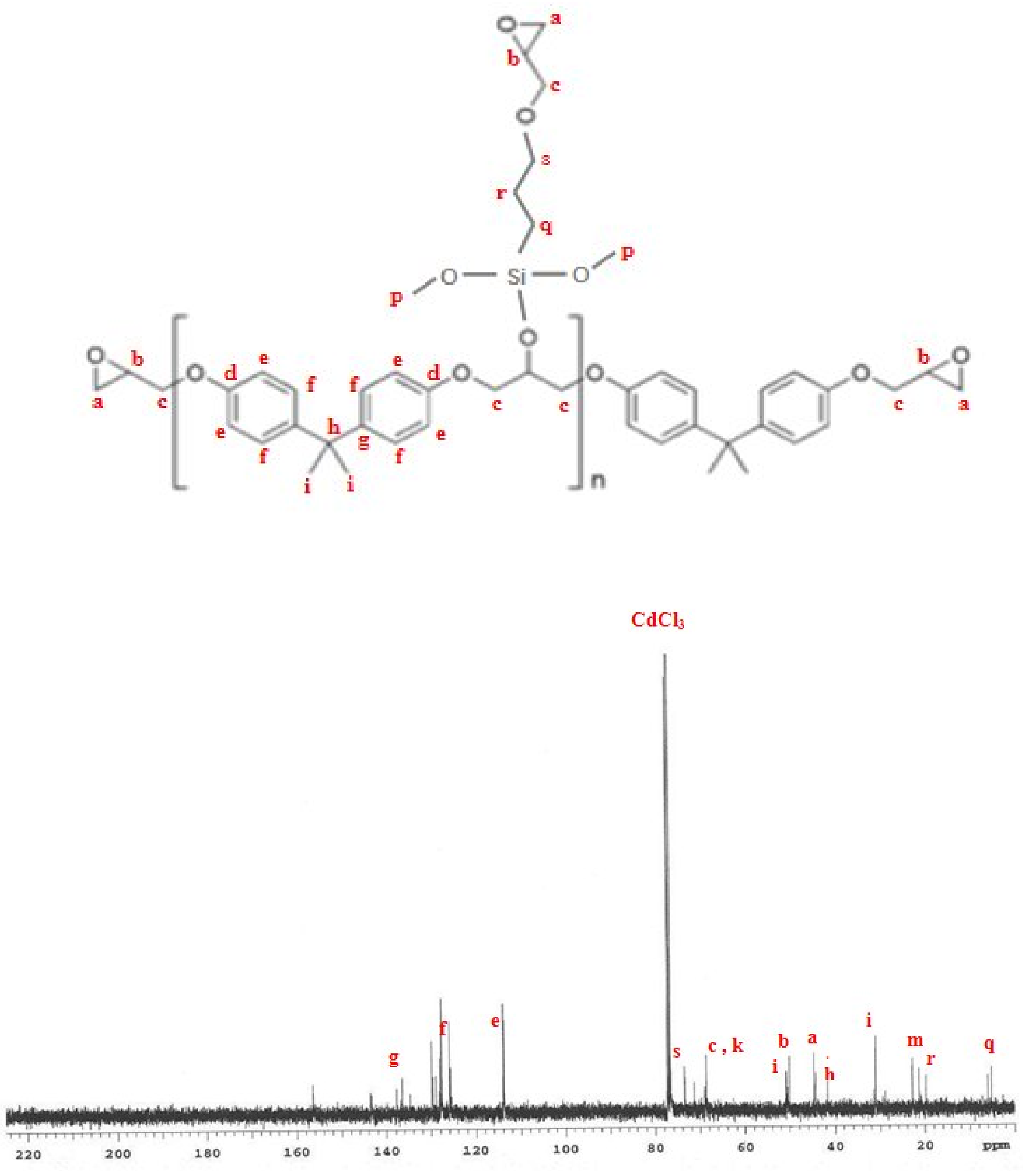


Figure 4.4. ^{13}C-NMR of Modified Epoxy

4.1.2. FTIR Analysis

FTIR spectroscopy was used to characterize the structure of pure epoxy resin and the modified epoxy resins

For pure epoxy resin, the band at 3500 cm^{-1} is assigned to –OH stretching. The bands at 2965 and 1383 cm^{-1} are characteristics of $–CH_3$ asymmetric and symmetric stretching, and the bands at 2877 and 1457 cm^{-1} are assigned to asymmetric and symmetric stretching mode of –CH2. The band at 915 cm^{-1} is the characteristic absorption of epoxide groups. The band at 1235 cm^{-1} is assigned to the ether bonds in epoxide groups. The absorption peaks at 1607, 1508 and 828 cm^{-1} are characteristics of substituted aromatic rings in epoxy resin (Figure 4.5).

The spectra of silane modified epoxy resins are very similar to that of pure epoxy resin, but some differences can still be detected. It is evident that the peak intensity at about 3500 cm^{-1}, corresponding to O–H stretching of the secondary hydroxyl in epoxy resin, decreases and even almost disappears after the silane modification. This indicates that the hydroxyl groups were consumed by the modification reaction, leading to a decrease in intensity of the absorption peak. In addition, after the silane modification the peak intensity at 1000–1100 cm^{-1} increases obviously due to the formation of Si–O–C bonds (Figure 4.6).

During the synthesis of γ-glycidoxypropyltrimethoxysilane modified epoxy polymer, every thirty-six minutes we got a sample for real time FTIR analysis. We could see the decreasing of O–H stretching of the secondary hydroxyl in epoxy resin and even almost disappears after the silane modification for every thirty-six minutes (Figure 4.7).

In addition, after the silane modification the peak intensity at 1000–1100 cm^{-1} increased obviously due to the formation of Si–O–C bonds for every thirty-six minutes (Figure 4.8).

These observations suggest that γ-glycidoxypropyltrimethoxysilane has been successfully grafted to epoxy polymer (Figure 4.9).

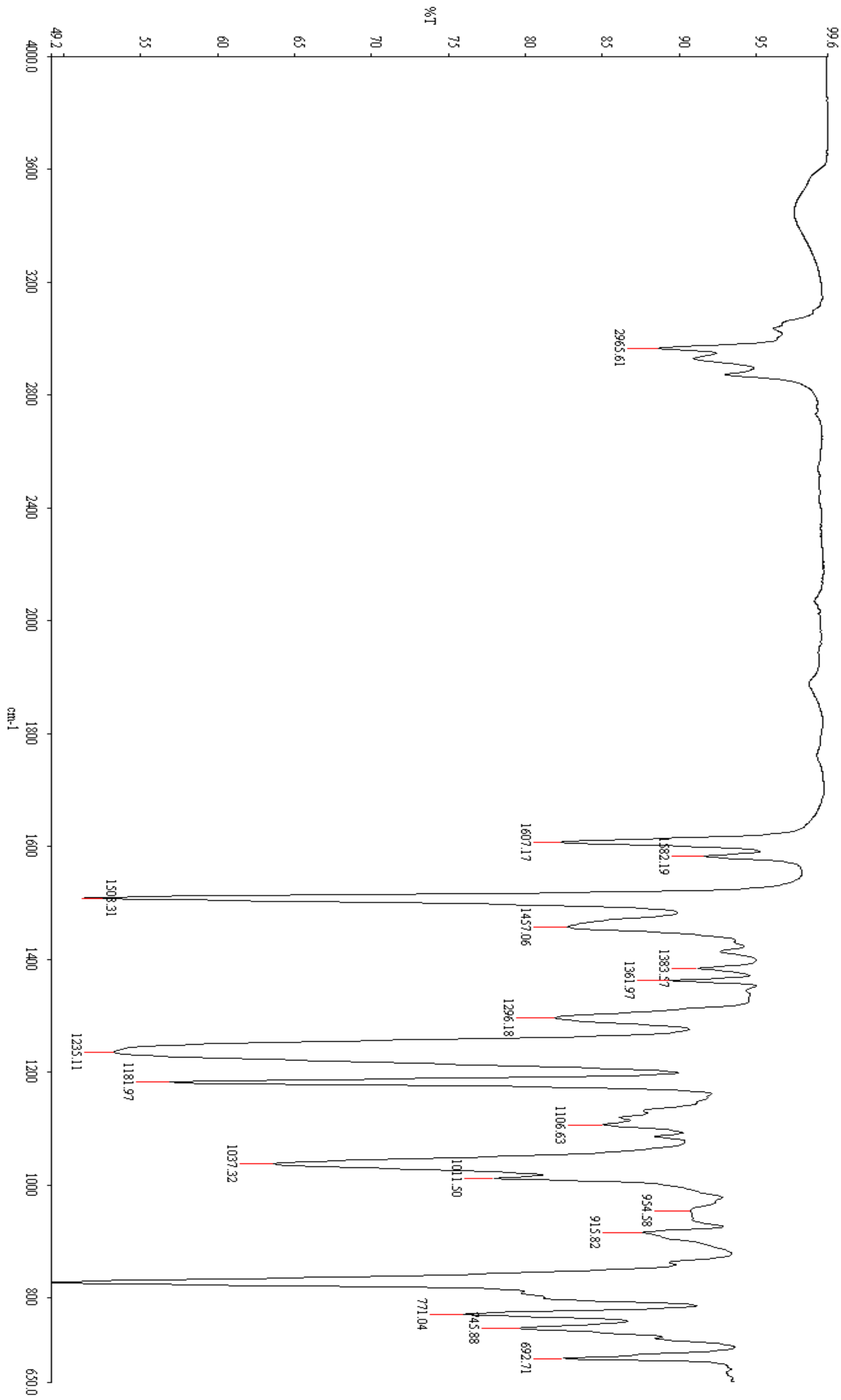


Figure 4.5. FTIR Spectrum of Epoxy Polymer

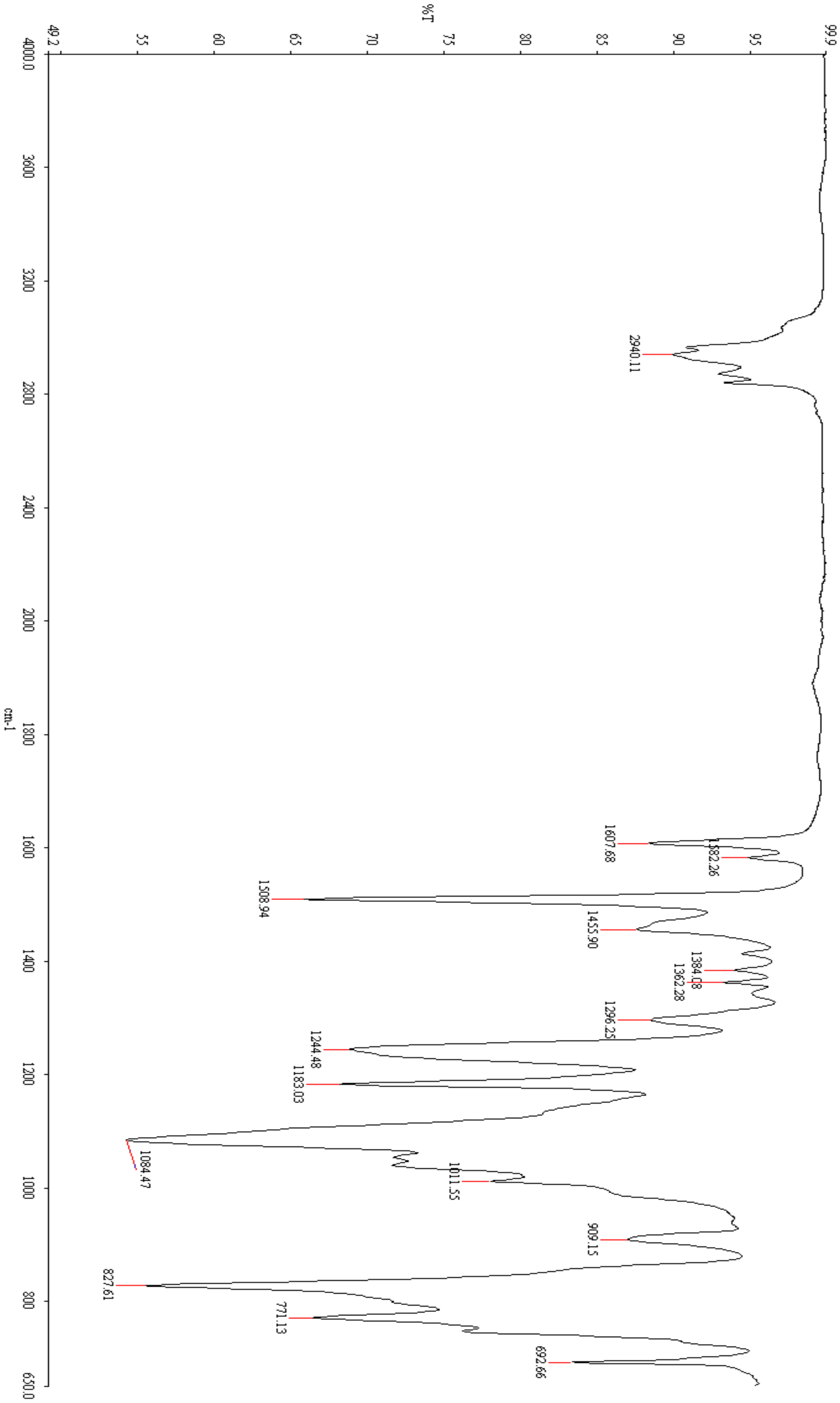


Figure 4.6. FTIR Spectrum of Silane Modified Epoxy Polymer

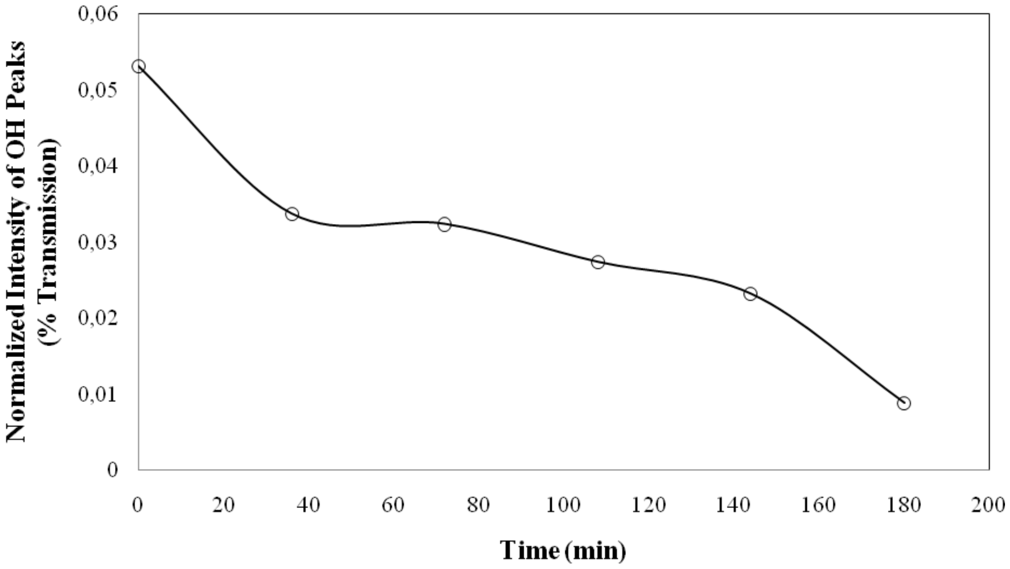


Figure 4.7. Change in Normalized Intensity of % Transmission of O-H

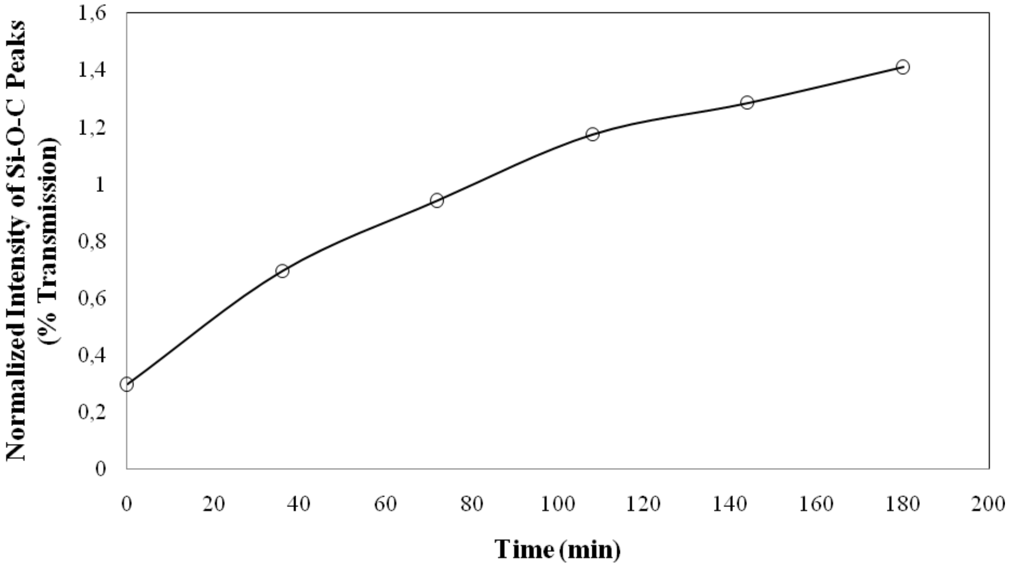


Figure 4.8. Change in Normalized Intensity of % Transmission of Si–O–C

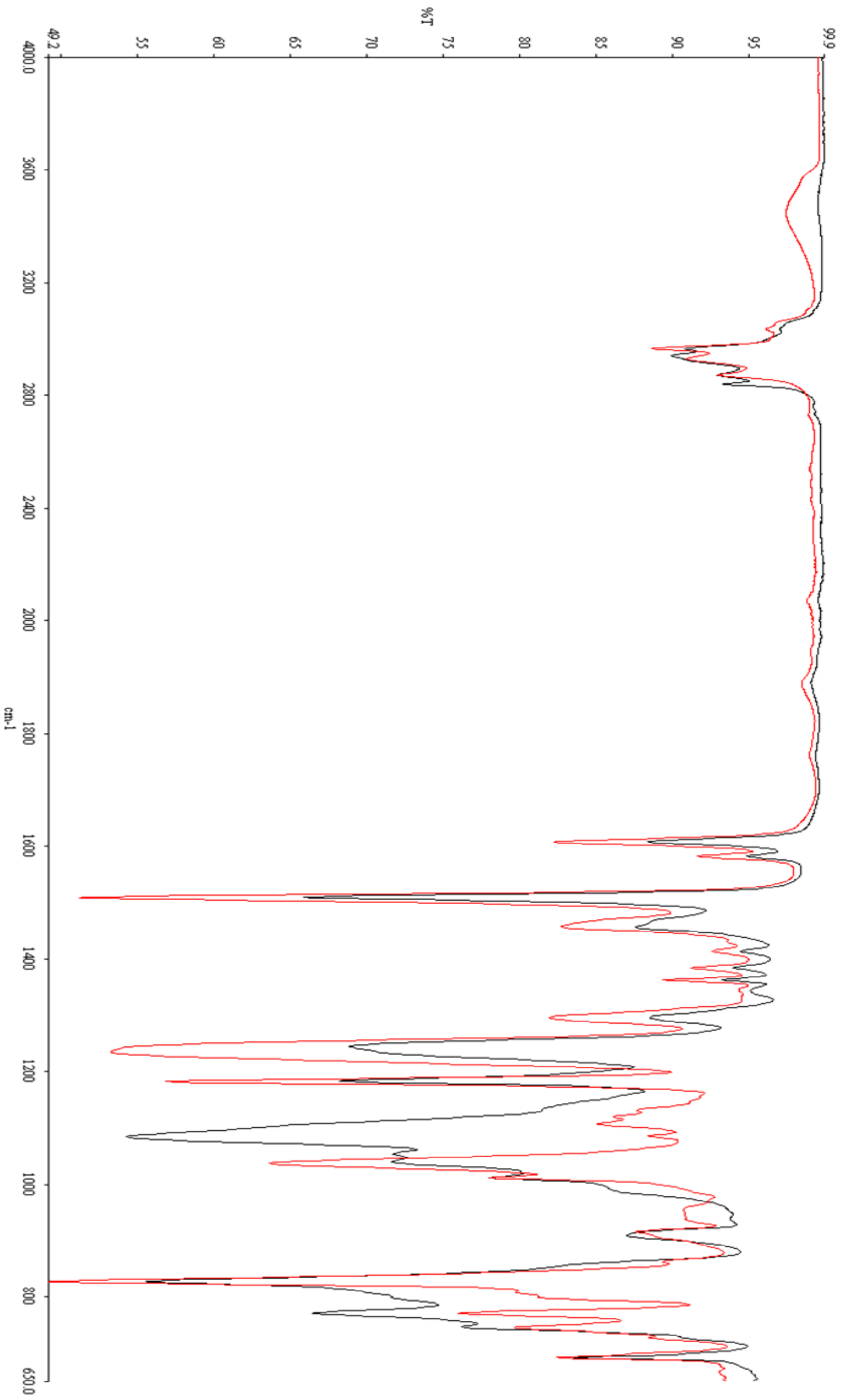


Figure 4.9. Modified and Unmodified Epoxy Polymer

4.1.3. Epoxide Equivalent Weight

E.E.W. value of epoxy polymer and γ-glycidoxypropyltrimethoxysilane modified epoxy polymer are given in Table 4.1.

Table 4.1. Properties of Unmodified and Silane Modified Epoxy Resins

Properties	Epoxy Polymer	Modified Epoxy Polymer
E.E.W.	660 g/eq	425 g/eq
Pendulum Hardness	196 Persoz	252 Persoz
# of MEK Double-Rub.	116	400
Surface Energy	46 Dyne	42 Dyne
Contact Angle Values	38°	42°

These data suggested that after modification, E.E.W. value decreasing. γ-glycidoxypropyltrimethoxysilane modified epoxy had 425 grams of resin that contains one molecule of an epoxy group (Figure 4.10). Pure epoxy had 660 grams of resin that contains one molecule of an epoxy group (Figure 4.11).

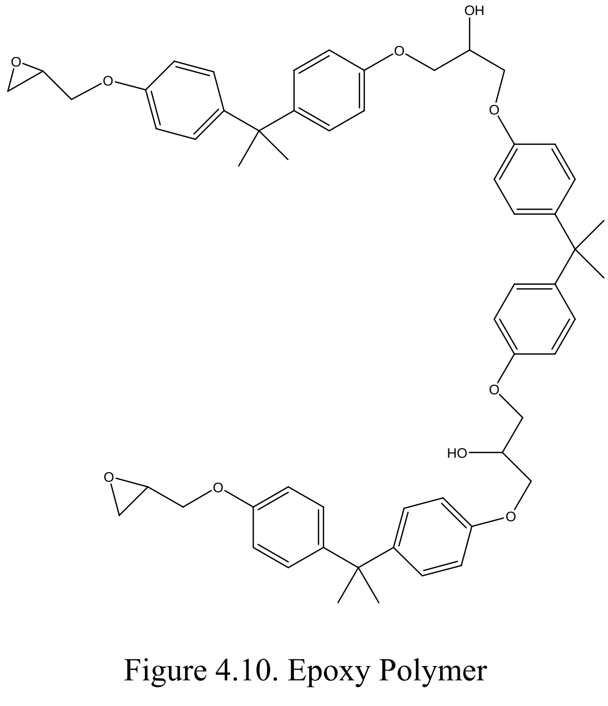


Figure 4.10. Epoxy Polymer

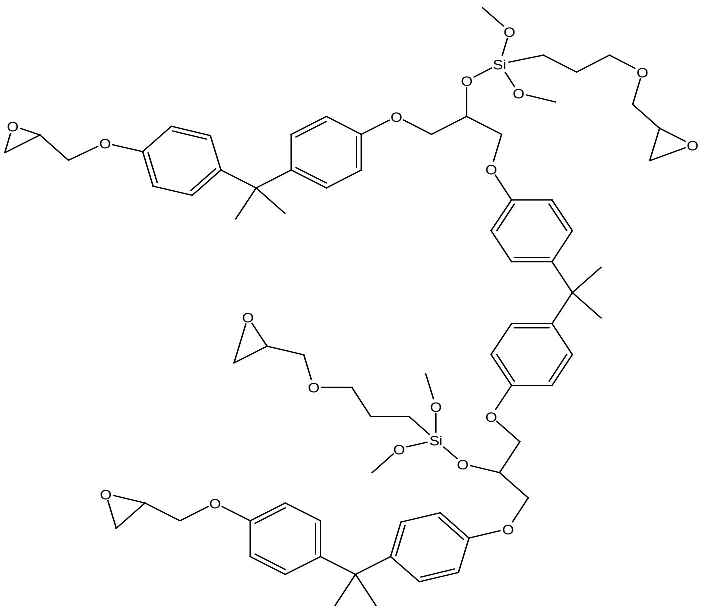


Figure 4.11. Silane Monomer Modified Epoxy Polymer

Decreasing of E.E.W. means that increasing epoxy functionality of polymer. Every epoxy functionality cures with amine's hydrogen and get more crosslink a three-dimensional polymer network. With increasing crosslink density, coating's barrier properties improves against for penetration of water and corrosive ion into the metal / coating interface that we will discuss in section 4.8. Corrosion performance.

4.1.4. Pendulum Hardness Test

Pendulum hardness test was also conducted to support the results to understand the degree of modification. The hardness values of test panels were given in the Table 4.1. These data shows that modification increases hardness. Since increasing epoxy functionality get more crosslink.

4.1.5. MEK Double-rub test

The MEK double-rub values of test panels were given in the Table 4.1. It is seen that MEK double-rub increases with modification. This is due to an increase in the epoxy functionality and therefore an increase in the degree of curing.

4.1.6. Surface Energy

The surface energy values of test panels were given in the Table 4.1. It is seen that modified epoxy had a lower surface tension due to the presence of Si atoms. It provides better oil, water and contamination repellency to the coatings.

4.1.7. Contact Angle Measurements

The contact angle values of test panels were given in the Table 4.1. Which are known to show the degree of hydrophobicity of solid surfaces or the degree of wetting ability. It is seen that the modified epoxy had a higher contact angle value which is the indication of higher hydrophobic properties compare to the pure epoxy. This result is a good agreement with the other results of this study. However, the degree of modification and therefore the hydrophobicity of surfaces are expected to depend on the conditions such as the amount of silane.

4.2. Corrosion Performance Tests on Epoxy Coatings

Corrosion performance tests were conducted to investigate the effect of silane modification on the product. The details of the test are given in Chapter 3 and the results obtained were interpreted by ASTM and ISO standards. These results were given in the Table 4.2. The degree of blistering of pure epoxy coating and the degree of corrosion around scribe of pure epoxy coating were given in Figure 4.12 a) and b). It is seen that hydrophilic hydroxyl group in the cured network made coating water loving, therefore a blister was observed on the surface and around scribe of coating. Since epoxy coating absorbs moisture and the diffusion of absorbed water into the epoxy–steel interface weakens the interfacial adhesion strength between epoxy and steel. This causes a corrosion that penetrates easily below coating layer (Figure 4.12 b)).

Table 4.2. Corrosion Performance of Pure Epoxy Coating

Features	**Test method**	**Limits**	**Results**
Degree of corrosion around scribe	ISO 4628-8	500 hours	8 mm
Degree of blistering	ASTM D 714	500 hours	No 4 medium

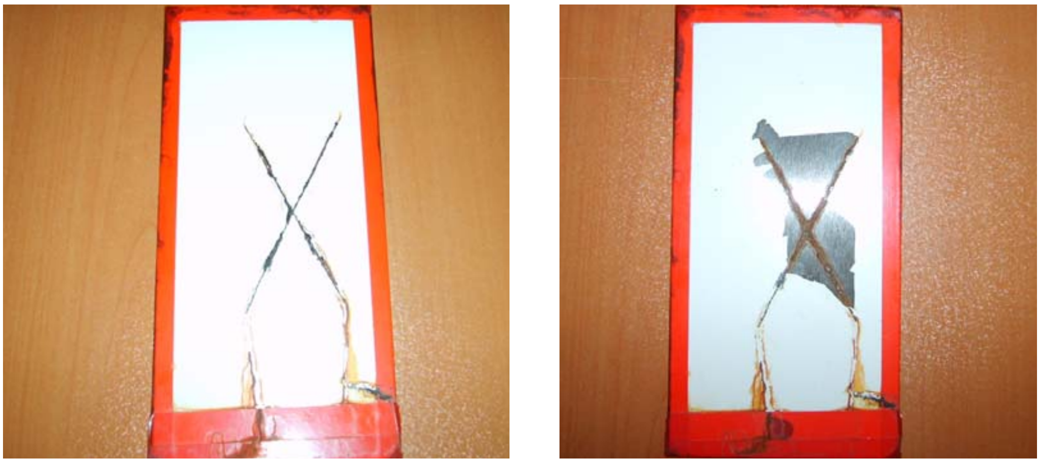
a) b)

Figure 4.12. a) Degree of Blistering of Pure Epoxy Coating b) Degree of Corrosion Around Scribe of Pure Epoxy Coating

The corrosion test results of silane modified epoxy coating, the degree of blistering and the degree of corrosion around scribe of coating were given in the Table 4.3 and Figure 4.13 a) and b). It is seen that no bilister was observed on the surface and around scribe of coating after silane modification due to higher hydrophobicity and water repellent characteristics of surface. Therefore, epoxy coating does not absorb moisture and no water diffuses into the epoxy–steel interface. This does not cause a corrosion that penetrates easily below coating layer, so the corrosion could not be penetrated easily below coating layer.

Table 4.3. Corrosion Performance of Modified Epoxy Coating

Features	Test method	Limits	Results
Degree of corrosion around scribe	ISO 4628-8	500 hours	1 mm
Degree of blistering	ASTM D 714	500 hours	No blister



a) b)

Figure 4.13. a) Degree of Blistering of Modified Epoxy Coating b) Degree of Corrosion Around Scribe of Modified Epoxy Coating

CHAPTER 5

CONCLUSION

In this study; commercial epoxy polymer was chemically modified by γ-glycidoxypropyltrimethoxysilane monomer under the catalysis DBTL organotin compound via the reaction between hydroxyl group in epoxy polymer and alkoxy group in silane aiming to enhance the corrosion performance of epoxy polymer.

Characterization results showed that γ-glycidoxypropyltrimethoxysilane has been successfully grafted to epoxy polymer. The results were;

- In the FTIR-ATR analysis; O–H stretching of the secondary hydroxyl in epoxy resin, decreases and even almost disappears after the silane modification, in addition after the silane modification the peak intensity at 1000–1100 cm^{-1} increases obviously due to the formation of Si–O–C bonds.
- In the NMR analysis; both ^{1}H-NMR and ^{13}C-NMR results depicted characteristic peaks of epoxy polymer and α-glycidoxypropyltrimethoxy silane modified epoxy polymer structures as shown in their molecular formula.
- In the other characterization tests, that E.E.W, contact angle, surface energy, MEK double-rub and hardness measurements were supported FTIR-ATR and NMR results.

Finally, the corrosion performance of modified and unmodified epoxy coatings was obtained. It was observed that γ-glycidoxypropyltrimethoxysilane modified epoxy polymer had a better corrosion performance against to the pure epoxy polymer according to ASTM B117.

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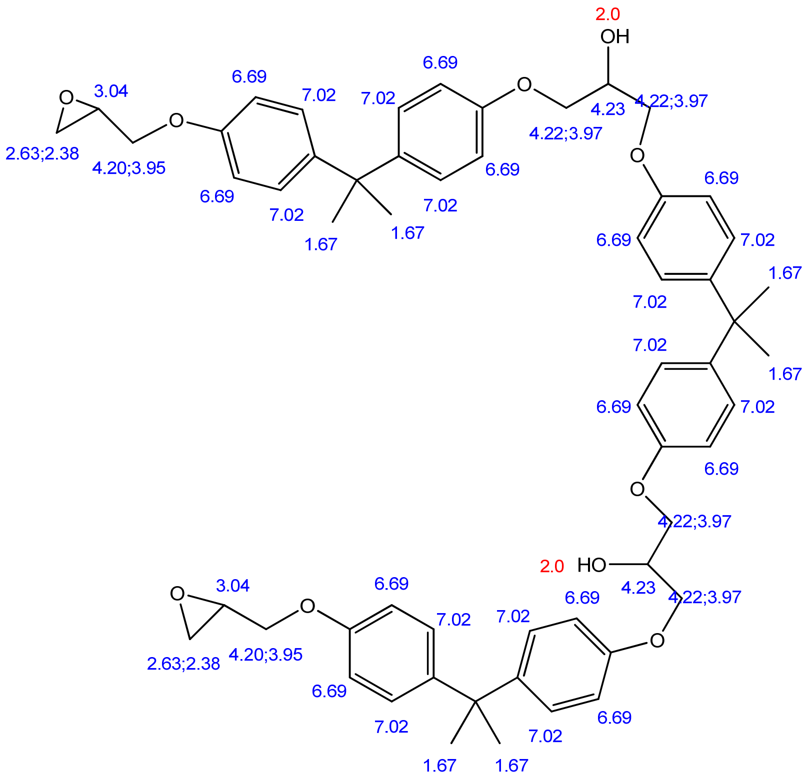
APPENDIX A

ESTIMATED NMR SPECTRUMS



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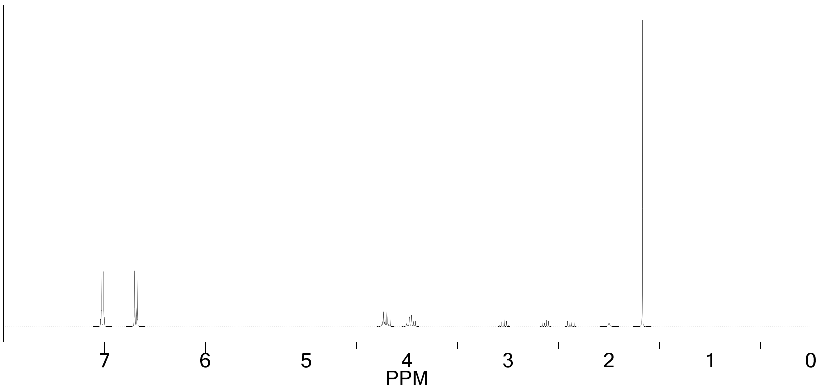
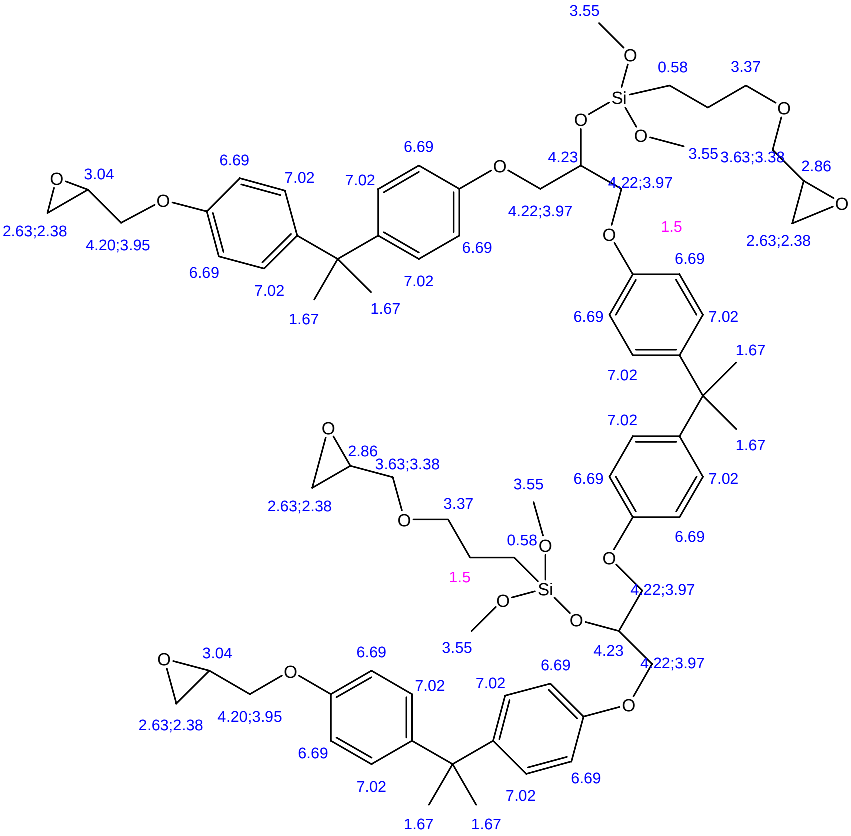


Figure A.0.1. ^{1}H-NMR of Pure Epoxy



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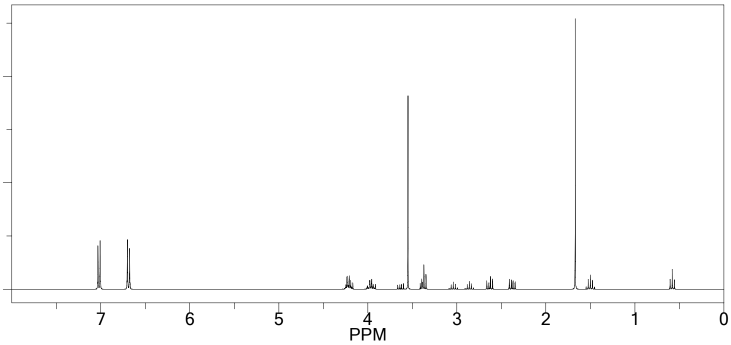


Figure A.2. ^{1}H-NMR of Silane Modified Epoxy

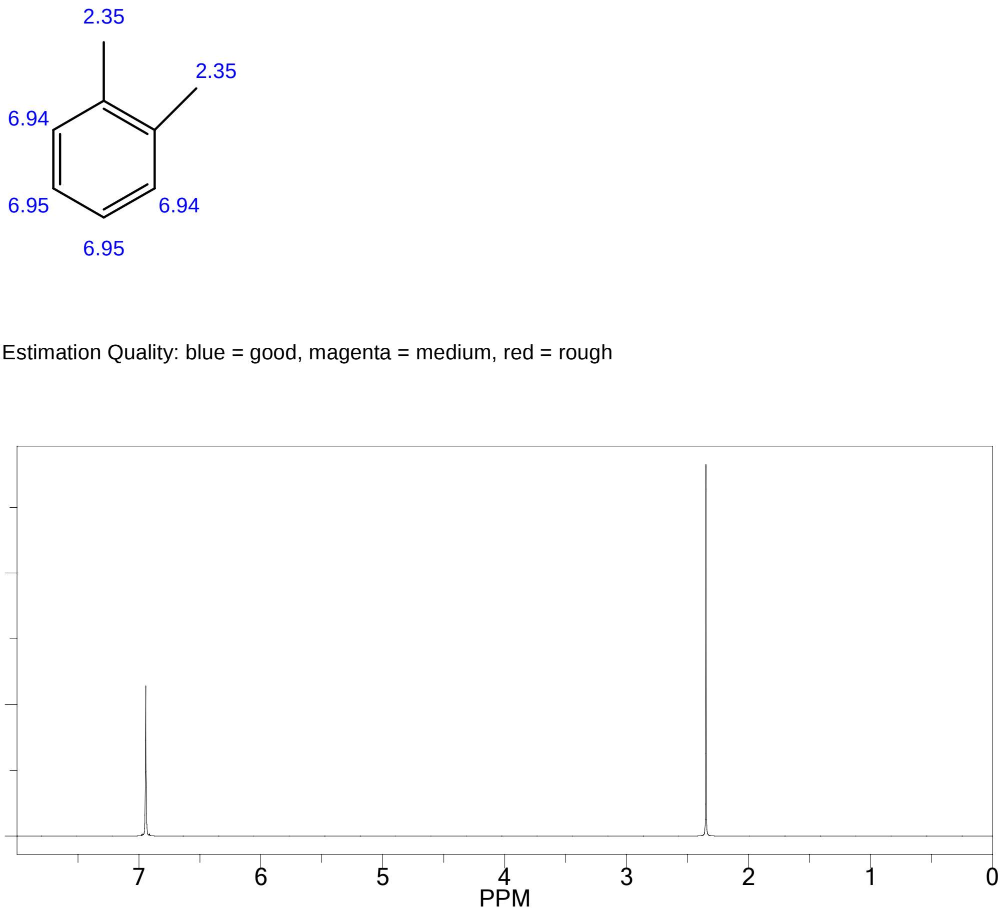


Figure A.3. ^{1}H-NMR of o-Xylene

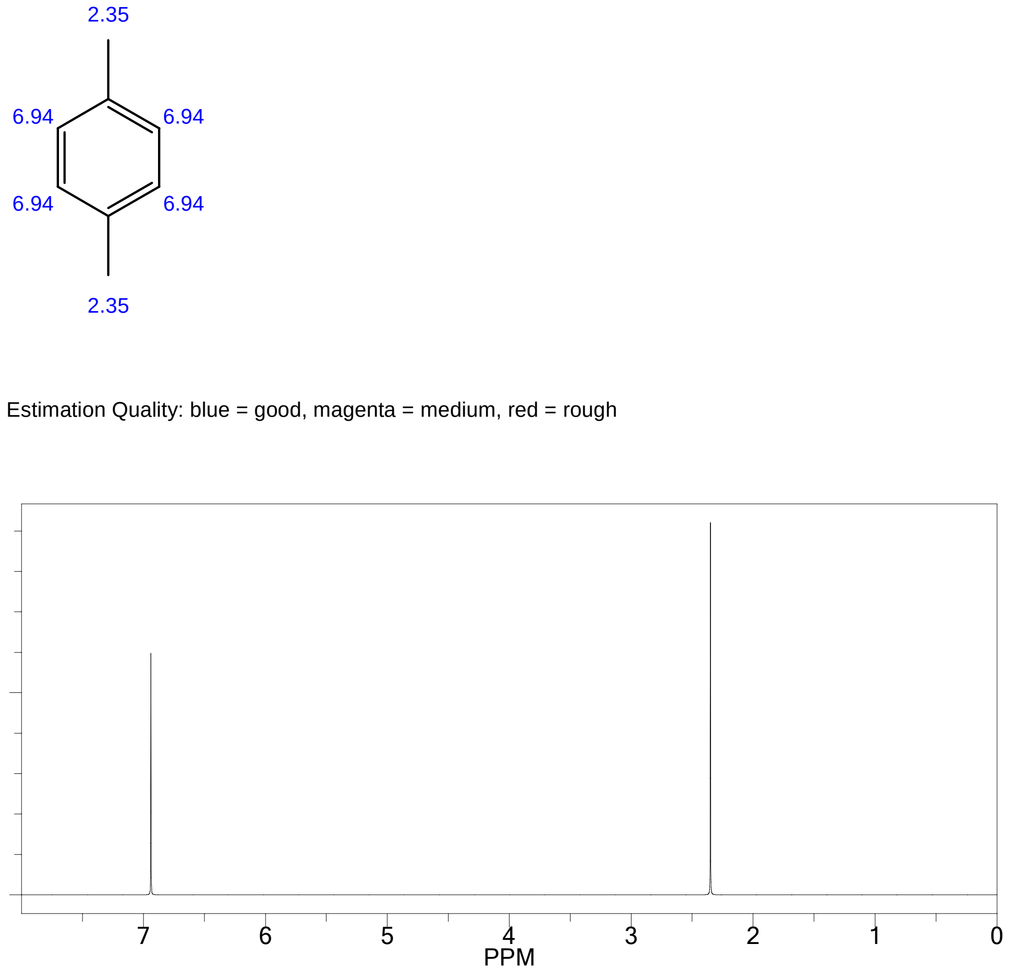
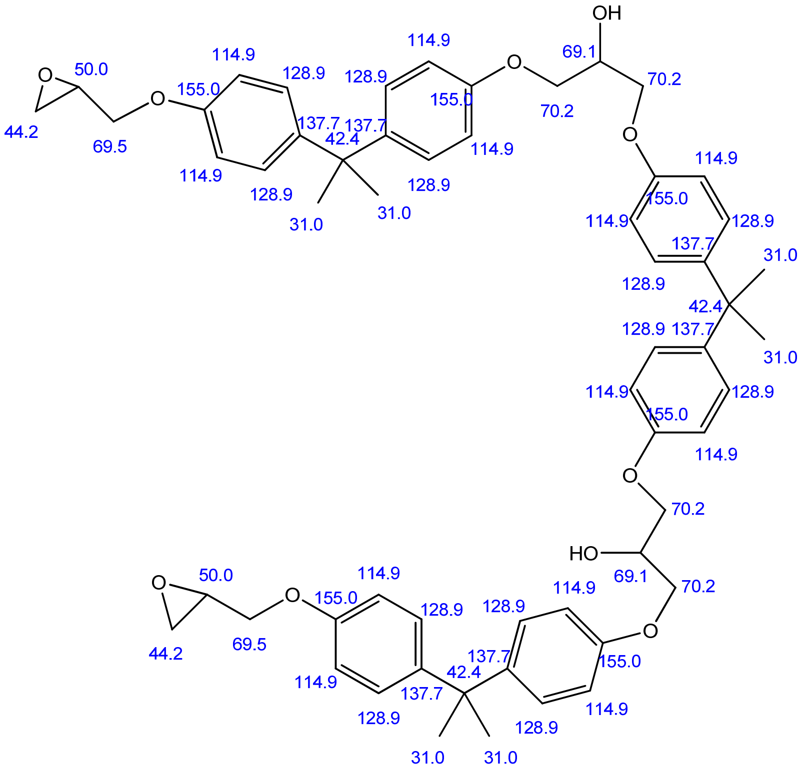


Figure A.4. ^{1}H-NMR of p-Xylene



Estimation Quality: blue = good, magenta = medium, red = rough

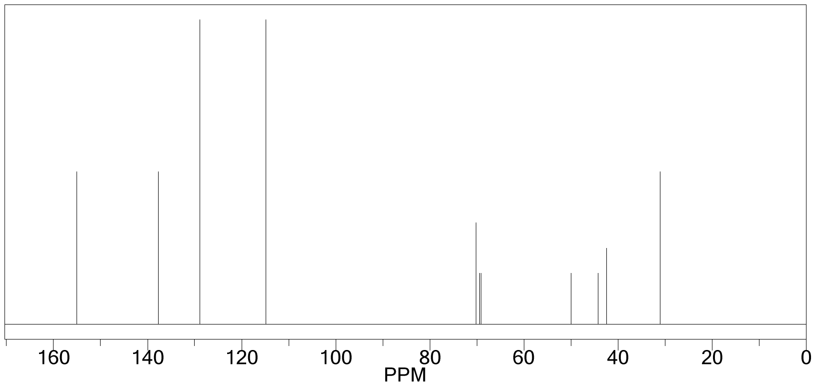
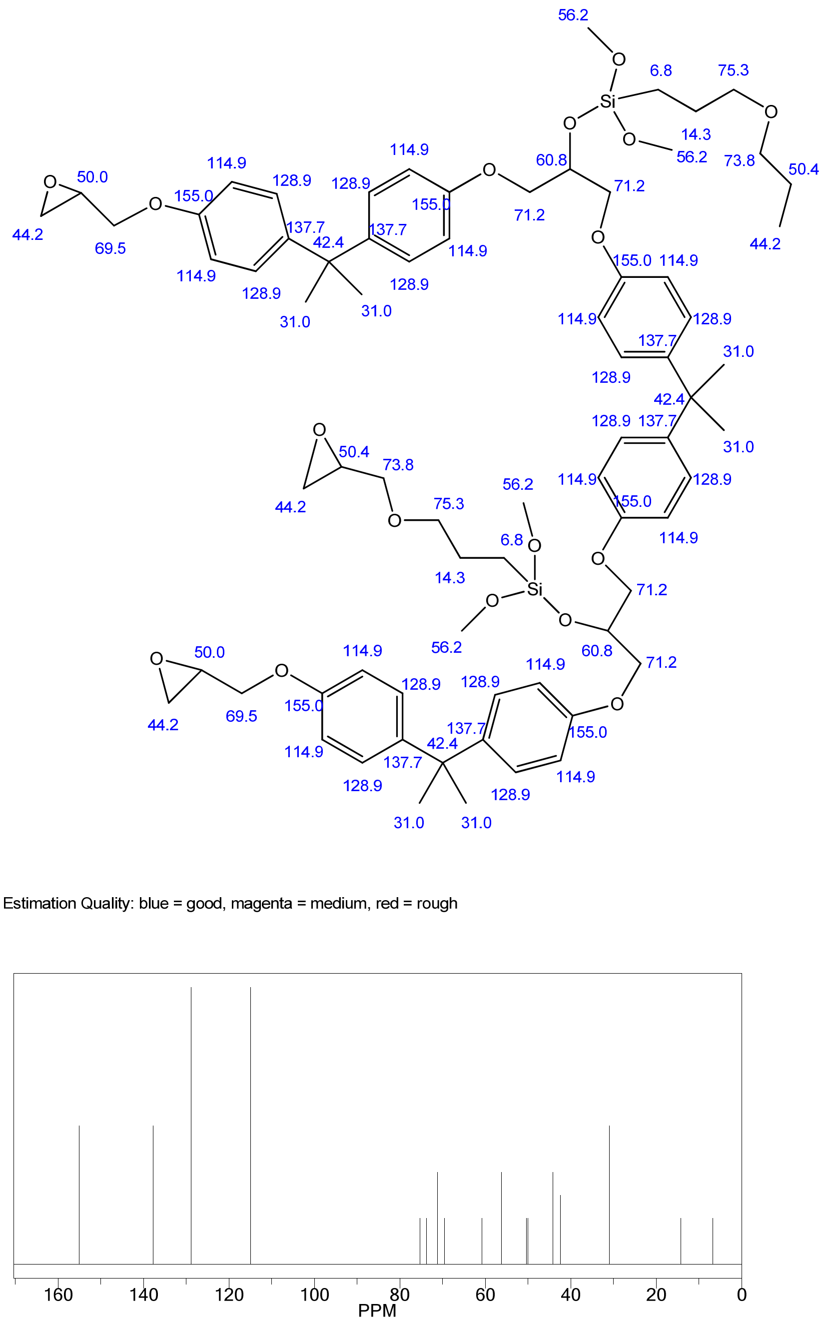
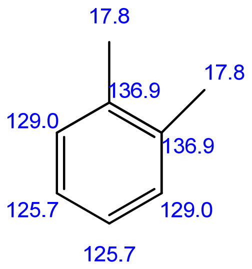


Figure A.5. ^{13}C-NMR of Pure Epoxy



Estimation Quality: blue = good, magenta = medium, red = rough

Figure A.6. ^{13}C-NMR of Silane Modified Epoxy



Estimation Quality: blue = good, magenta = medium, red = rough

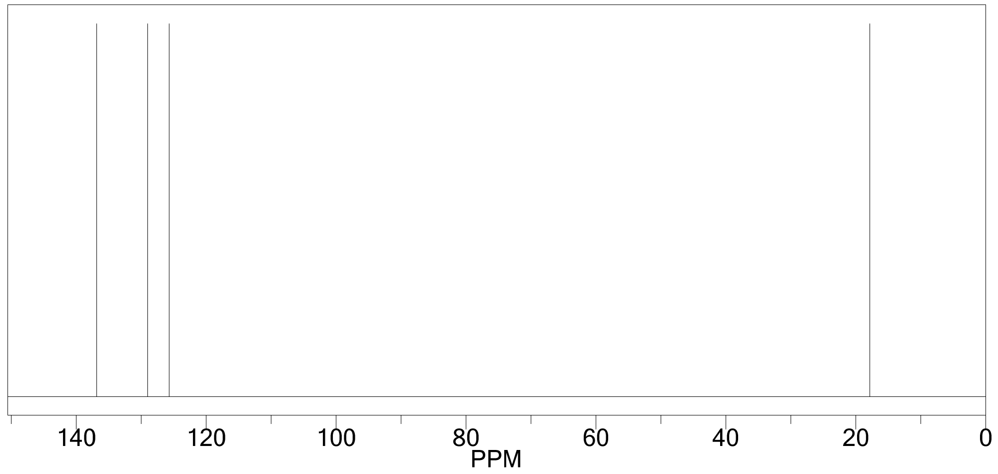


Figure A.7. ^{13}C-NMR of o-Xylene

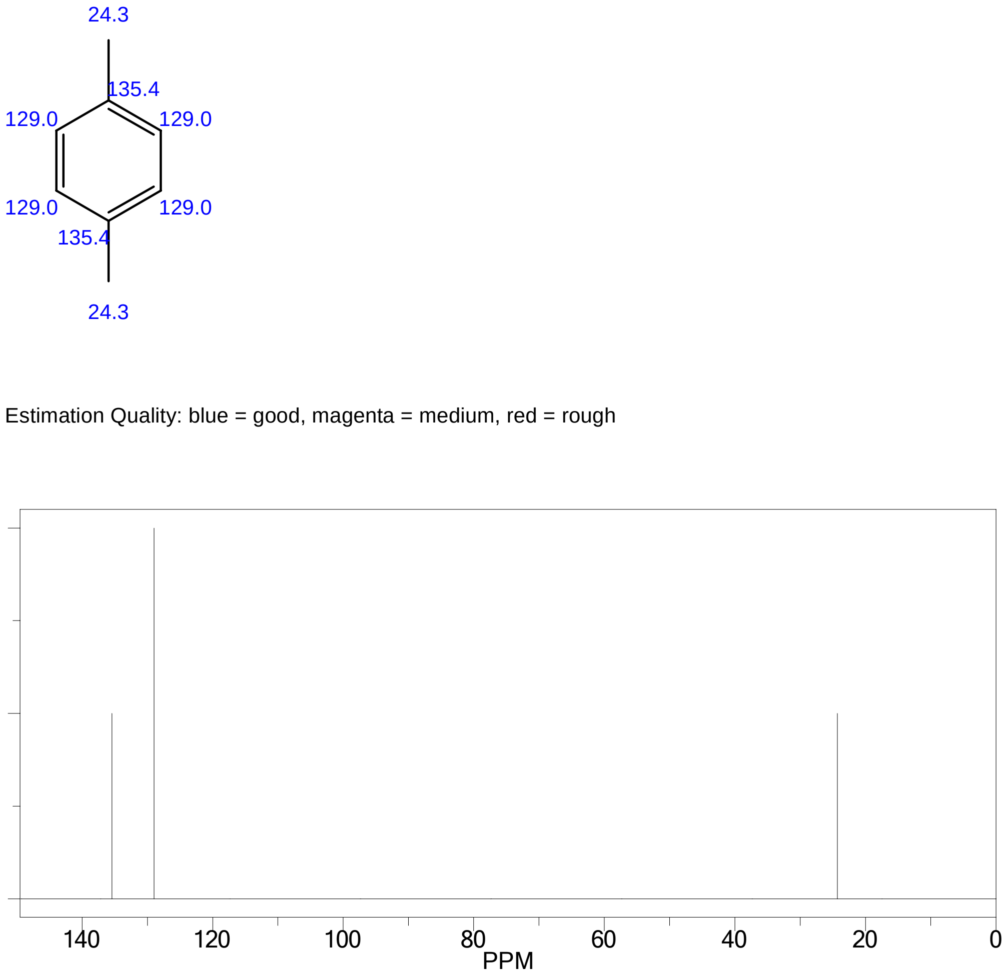


Figure A.8. ^{13}C-NMR of p-Xylene