

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Epoxy Resin

Epoxy resin is thermosetting plastics containing an epoxide group. Epoxy resin systems have been found many uses in building, industrial maintenance paints and civil engineering applications. Epoxy systems can be formulated to meet almost any contingency, which is required when, for example, concrete needs to be bonded, repaired, protected, surfaced or resurfaced and sealed or decorated. All these epoxy systems can be applied on buildings above or below ground, on road and bridge construction and even underwater. The principal characteristics of epoxy resin systems provide an excellent combination of properties of high value in the construction industry and coating formulation. These properties include [4]:

- High strength adhesion to most building materials
- Excellent abrasion resistance
- Very low shrinkage during and after curing
- Good chemical resistance
- Excellent toughness, hardness and flexibility

Epoxy resin contains one or more reactive epoxy groups. The basic liquid epoxy resin consists of bisphenol A (BPA) epoxides made by reacting BPA with epichlorohydrin (ECH). Under basic conditions, the initial reaction is a formation of BPA anion (BPA^-), which attacks ECH and results in the formation of new oxirane

ring with elimination of chloride anion (Cl^-). The reaction of BPA with NaOH and ECH gives the diglycidyl ether of bisphenol A (DGEBA) [5, 6] (as shown in Figure 2.1).

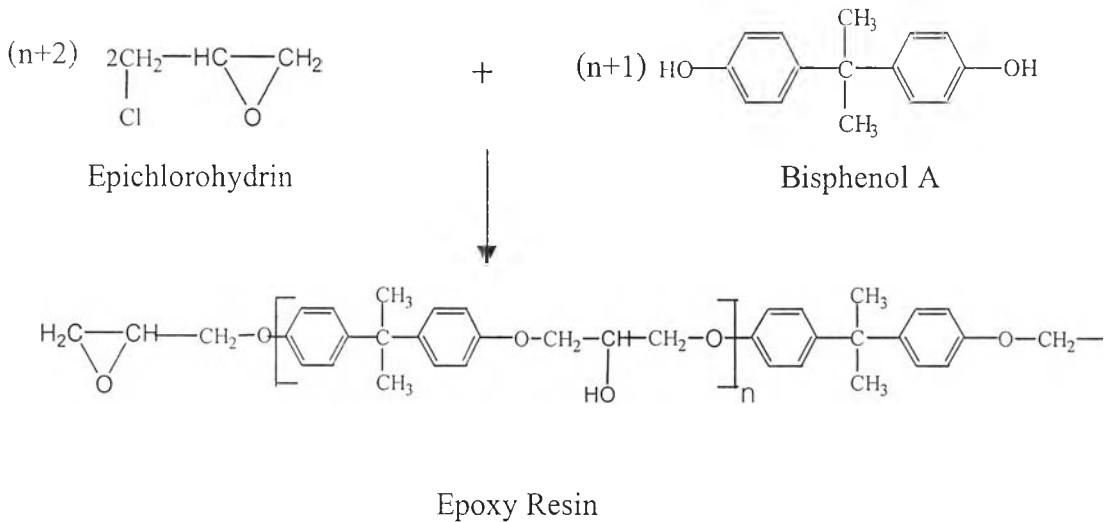


Figure 2.1 Standard bisphenol A – based epoxy resin

Side reaction (hydrolysis of epichlorohydrin, reaction of epichlorohydrin with hydroxyl groups of polymer) as well as the stoichiometric ratio need to be controlled to produce a prepolymer with two epoxide end groups. The polymer may be represented by the following general formula, where the molar ratio of ECH/BPO determines the average n value; $\text{ECH/BPO} = (n+2)/(n+1)$. The molecular weight of the polymer is controlled by the ratio of ECH/BPO [7]. Epoxy resins are characterised by their Epoxide Equivalent Weight (E.E.W.), which is defined as, the weight of resin containing one gram equivalent of epoxide. The E.E.W. is also referred to as, Weight Per Epoxide (W.P.E.) or Epoxy Molar Mass (E.M.M.). All three terms are interchangeable. Most epoxy resins used in surface coating systems have equivalent weights (E.W.W.) between 180 and 3,200, which are mainly in “two-package” low temperature cure systems.

Table 2.1 Characterization of commercial epoxy resin

n value	Molecular Weight	E.E.W.	Melting Point (°C)
0 - 1	350-600	170-310	< 40 °C
1 - 2	600-900	310-475	40-70 °C
2 - 4	900-1,400	475-900	70-100 °C
4 - 9	1,400-2,900	900-1,750	100-130 °C
9 - 12	2,900-3,750	1750-3,200	130-150 °C

Epoxy resin coating obtains their excellent properties through reaction with curing agents. The curing agent reacts with the epoxide groups and/or hydroxyl groups of the epoxy resin. The curing agent is either an amine or an amide. All are capable of undergoing crosslinking reaction with the epoxy resin to form tough resistant cross linked films, which give outstanding protection and adhesion. These are normally two-pack systems and the amine is kept apart from the epoxy resin until just before use.

Curing reactions of epoxy resins (DGEBA) with amine form cured epoxy. Primary aliphatic amine reacts at room temperature with the epoxide group, forming secondary amines, which are capable of further reaction with another epoxy group to form a tertiary amine link between two epoxy resin molecules (as shown in Figure 2.2).

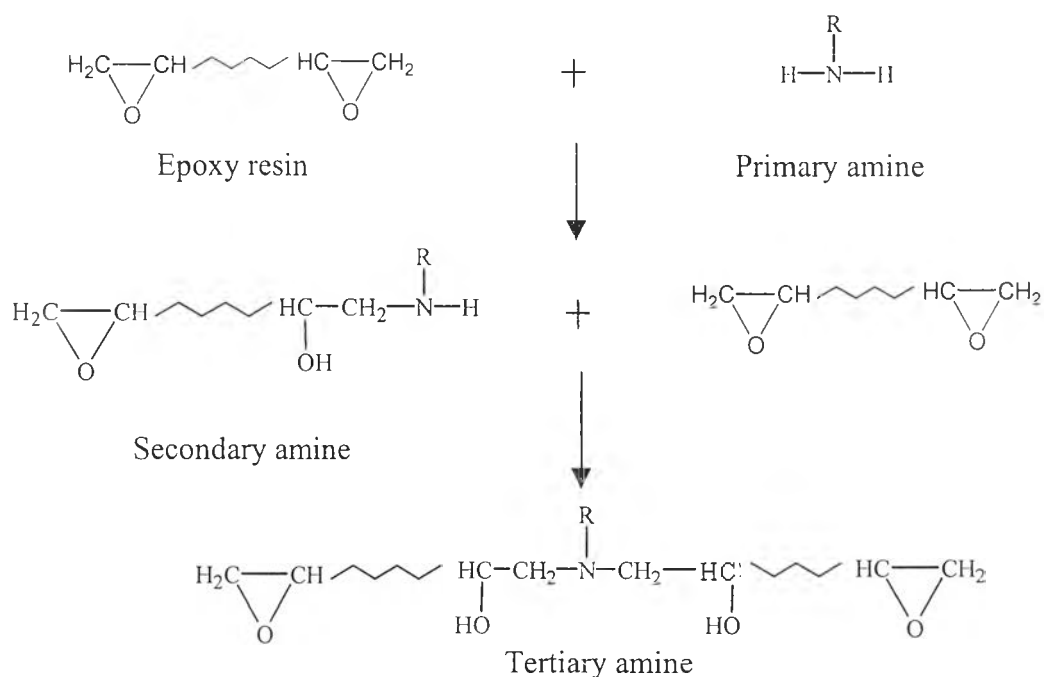


Figure 2.2 Reaction of an epoxy resin and amine

Thus a complex, high molecular weight structure is achieved when both reactions occur during epoxy resin is cured. In practice, primary aliphatic diamine are too volatile to be satisfactorily used as a curing agent, however; it will be a high molecular weight structure if it is reacted by polyamine such as diethylenetriamine (DTA) [4] (as shown in Figure 2.3).

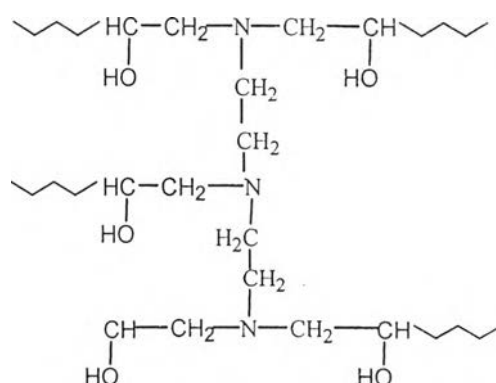


Figure 2.3 Epoxy polyamine reaction

Epoxy resins used in coating formulations have properties include good chemical resistance, outstanding adhesion to a variety of substrates, excellent toughness, hardness and flexibility. However epoxy based coating and flooring do not have good resistance to weathering in sunlight resulting in a surface degradation phenomenon known as chalking, which changes both gloss and color. The ways to improve properties of resin by protective coating are typically top-coated with a more weatherable coating, i.e. vinyl or aliphatic polyurethane coating. The end result is a two or sometimes three coat system, but it is also labor intensive and expensive to apply.

2.2 Silane Coupling Agent

Organofunctional silanes may be used as adhesion promoters between organic polymers and mineral substrates. The silanes adhesion promoter, or “coupling agent” may function as [8];

(1) A finish or surface modifier may theoretically be only a monomolecular layer, but in practice it may be several monolayers thick.

(2) A primer of size is generally 0.1 to 10 μm thick, and must have adequate mechanical film properties, such as rigidity, tensile strength, and toughness to carry the mechanical load when the composite is stressed.

(3) An adhesive depends on the thickness of the bonding material at the interface.

Silane coupling agents are used to improve the bonding between the reinforcing phase and the polymer. The ability of silane added to a coating formulation to migrate to the substrate interface and improve bonding, silanes have been added to latices and hydrolyzed to form an interpenetrating polymer network (IPN). A silane containing at least one carbon–silicon bond is known as an organosilane. The organic groups attached to the silicon atom can be either reactive or non-reactive. They have the

general structure of $R_nSiX_{(4-n)}$, when R is a nonhydrolyzable organic moiety that can be either an alkyl, aromatic, organofunctional or a combination of any of these groups. These groups provide the organic compatibility, which allows the silane to form IPNs, or in the case of a reaction of organofunctional silane to co-react with the coating polymer. Alkyl and aryl silanes are utilized to improve gloss, hiding power, mixing time and other properties. The X represents alkoxy moieties, most typically methoxy or ethoxy, which reacts with various forms of hydroxyl groups and liberates methanol or ethanol. These groups can provide the linkage with inorganic substrate [8 -10].

The reaction of silane can be described by Figure 2.4. First, the alkoxy group of silane will be hydrolyzed by water from an external source or may come from the water at the substrate to silanols, which spontaneously condense to yield silanol oligomers. After that, the silane will be coupled onto a substrate surface with a loss of water. Condensation polymerization of silanol molecules may be more rapid when these molecules are adsorbed on an oxide surface than when they are in solution or in a precipitated form. Siloxane network and surface siloxane bond formation are accelerated by heat and dehydration of the hydrogen bonded adsorption complex [11,12].

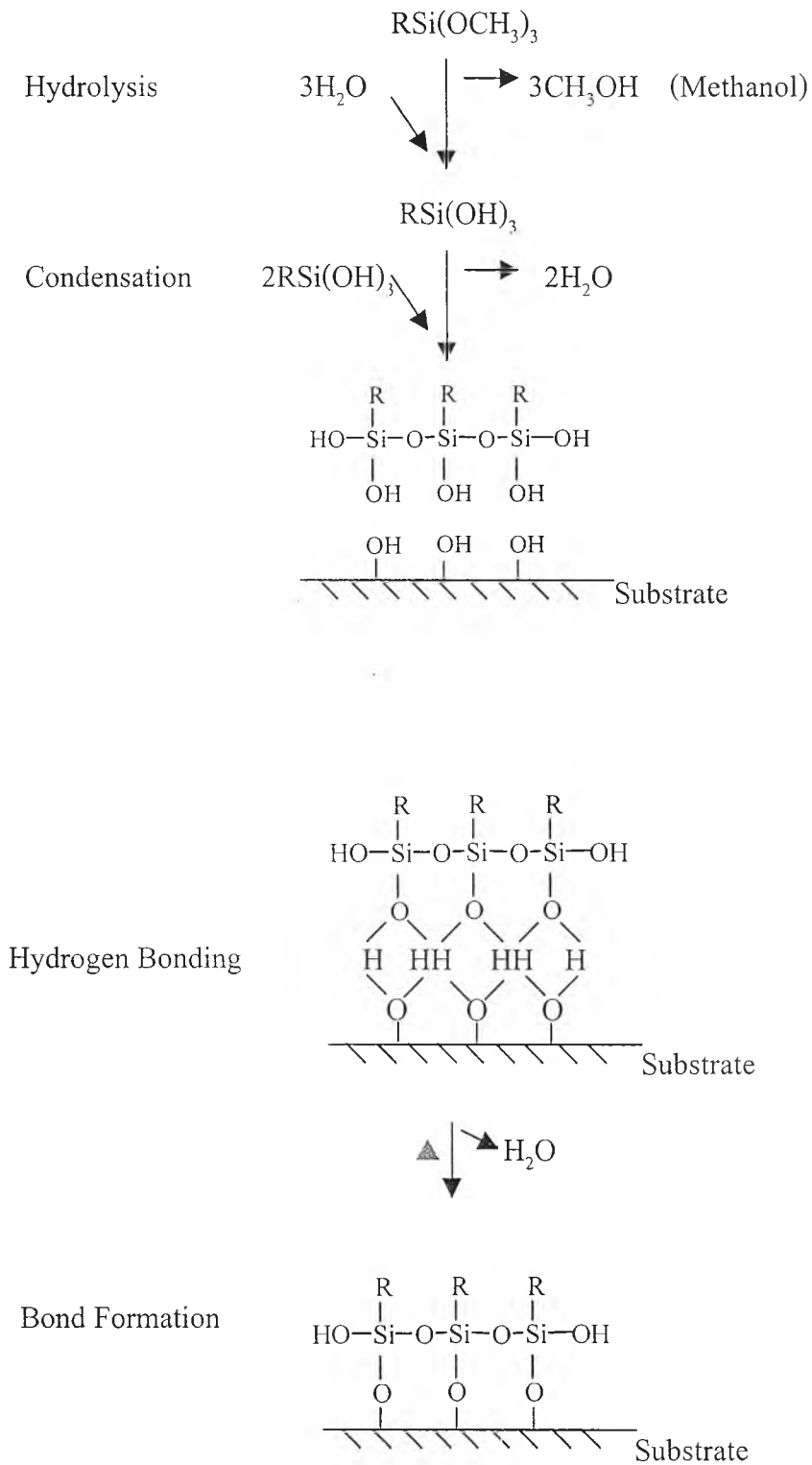


Figure 2.4 Reaction of the silane coupling agent [12]

Table 2.2 Representative commercial silanes

Organofunctional Group	Chemical structure	Abbreviations
Vinyl	$\text{CH}_2=\text{CHSi}(\text{OCH}_3)_3$	VS
Chloropropyl	$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	CPS
Epoxy	$\begin{array}{c} \diagup \text{O} \diagdown \\ \text{CH}_2-\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3 \end{array}$	GPS
Methacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}-\text{COOCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3 \end{array}$	MPS
Primary amine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$	APS
Diamine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	AEAPS
Mercapto	$\text{HSCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	MGPS
Cationic styryl	$\text{CH}_2=\text{CHC}_6\text{H}_4\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3 \text{HCl}$	CSS

2.3 Color Difference of Film using a Colorimeter

Methods of measuring color by using a colorimeter gives three numbers, which represent hue, intensity and value. The hue is the basic color (e.g., orange, green or blue). The intensity, also called chroma, saturation or color strength, refers to the

concentration or dilution of the color. Value is the lightness or darkness of the color. The $L^* a^* b^*$ color space is presently one of the most popular color spaces for measurements of object color by Hunter Associates Laboratory in 1947. In this color space, L^* indicates lightness and a^* and b^* are the chromaticity coordinates. The a^* and b^* indicate color directions : $+a^*$ is the red direction, $-a^*$ is the green direction, $+b^*$ is the yellow direction, and $-b^*$ is the blue direction. The center is achromatic as the a^* and b^* values increase and the point moves out of the center, the saturation of color increases [13] (as shown Figure 2.5).

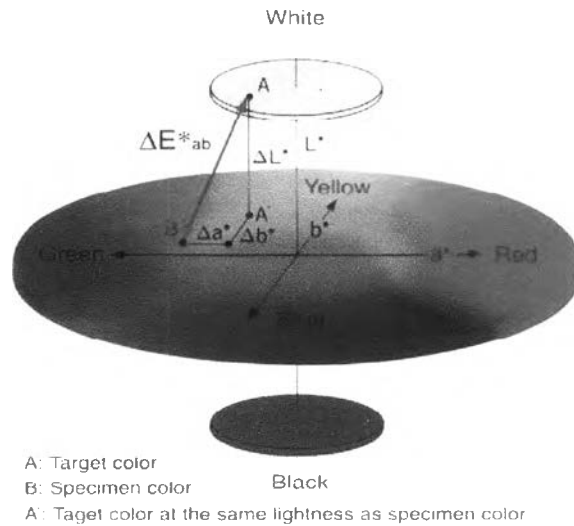


Figure 2.5 Color difference in the $L^* a^* b^*$ color space

Color difference ΔE^* in the Hunter Lab color space, which indicates the degree of color difference is defined by the following equation;

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (2.1)$$

where ΔL^* , Δa^* , Δb^* ; Difference in L^* , a^* and b^* values between the specimen color and the target color.

2.4 Film Resistance to Salt Spray

This method is used for testing dry films, the test is also applicable to corrosion resistance. It is well established that salts such as sodium chloride can cause rapid corrosion of ferrous substrate, and it is useful to have information of behaviour of a particular system in protecting such a substrate from corrosion both with intact and damaged paint films.

The corrosion tester typically operates as a conventional salt spray.

- Corrosion solution from the internal reservoir is pumped to the nozzle where it mixes with compressed air.
- Nozzle atomizes solution and air into corrosion fog.
- Chamber heater maintains the programmed chamber temperature.

Two tests are in common use: the continuous and the intermittent salt spray tests.

The continuous test: a continuous fog of salt solution is wafted from a nozzle in a special corrosion-resistant chamber to test the ability of coating to balk corrosion of metal. The test is of the 'pass' or 'fail' type, whereby the coating is subjected to treatment for a specified time and then examined for failure. Care must be exercised in interpreting the results of the test; it is not intended to be used as an accelerated test for normal weathering. The panels are prepared by the method described in ASTM D 609. The back and the edges of the panel are coated with a good protective air-drying material, tape or wax. The panel is aged for 24 hours before starting the test. A salt mist is produced by spraying a synthetic sea-water solution through an atomizer. The solution, which drains from the test panels is not recirculated. Panels are examined, rinsed in running water and dried with absorbent paper and examined immediately for blistering, adhesion, and corrosion from the cut. The use of standardized evaluation techniques, giving numerical ratings to test specimens is a common practice in paint

testing. Rating systems for the evaluation of corrosion and blistering on coated metal panels have been standardized as follow [2, 14, 15]:

- (1) ASTM D 610: Evaluating Degree of Rusting on Painted Steel Surfaces.
- (2) ASTM D 714: Evaluating Degree of Blistering of Paints.
- (3) ASTM D 1654: Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments.

The intermittent salt spray test is similar to the continuous test except the mist is produced each day for 8 periods of 10 minutes at intervals of 50 minutes. It is carried for 5 consecutive days and then 'rested' for 2 days. It is normally confined to government contract specifications and is clearly not as severe as the continuous salt spray method.

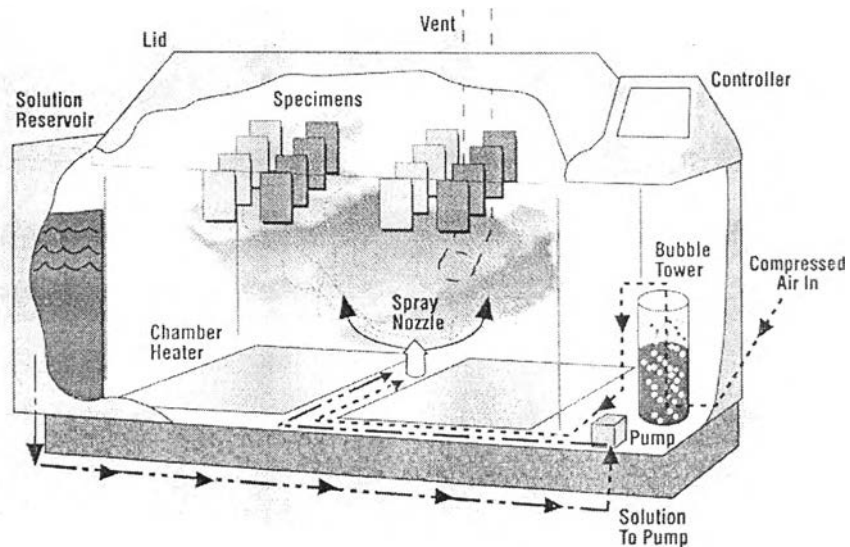


Figure 2.6 Salt spray

2.5 Mechanical Properties of Flooring Paints

The testing for mechanical properties is to effectively evaluate their function of substrate protection and/or improved appearance. Mechanical tests are usually carried out with the coating intact on the substrate. The testing of mechanical properties in many cases related to the end use of the paint, has resulted in the establishment of standard tests.

2.5.1 Adhesion Test

The most common test of adhesion is the crosscut adhesion test. A series of parallel cuts made into a coated surface in a systematic measure are used to rate adhesion of the material to its substrate [1]. In version A, an x cut is made in the film to the substrate. In version B, a lattice pattern with either six or 11 cuts, one or two millimeters apart, in each direction is made in the film to the substrate, pressure sensitive adhesive tape is firmly pressed over the grid and pulled quickly to increase the severity of the test [3,16]. The number of squares that have coating remaining is evaluated by comparison with description and illustration in Appendix A (ASTM D 3359 Tape test).

2.5.2 Hardness Test

Hardness is a quality measurement for solidity and firmness. Durometers, the measuring instrument, come in various types; therefore, the selection of durometers depends on the material to be measured. The type A durometer is used for soft rubber and non-rigid plastics, while the type D is used for harder rubber and plastics (ASTM D 2240). All durometers differ primarily in the sharpness of the point of the conical steel indenter and the magnitude of the load applied to the indenter by a calibrated spring, the type D having the sharpest and most heavily loaded indenter [1, 17]. The

durometer measures hardness based on the depth of indentation; the hardness varies from 100 at zero indentation to 0 at an indentation of 0.100 in (2.54 mm) and is automatically indicated on a scale. The load acting on the indenter usually varies inversely with the depth of penetration, being a maximum at zero penetration and reducing to practically zero load at maximum penetration, although some durometers use a weight to apply a constant load. Results obtained with one type of durometer cannot be correlated with those obtained with another type.

2.5.3 Compressive Strength

Compressive properties describe the behavior of a material when it is subjected to a compressive load. Loading is at a relatively low and uniform rate. Compressive strength and modulus are the two most common values produced. The specimen is placed between compressive plates parallel to the surface. The specimen is then compressed at a uniform rate. The maximum load is recorded along with stress-strain data. An extensometer attached to the front of the fixture is used to determine modulus. The specimen size is prepared by the method described in ASTM C 579.

Compressive strength and modulus are the two useful properties obtained.

$$\text{Compressive strength} = \frac{\text{maximum compressive load}}{\text{minimum cross-sectional area}} \quad (2.2)$$

2.6 Literature Review

For many years now, epoxy coating and flooring have been used in a wide range of protective coating for steel, aluminum and concrete in maintenance, marine, construction and finishing product. However, epoxy based coating and flooring generally do not have good resistance to weathering in sunlight, while such coating

maintains their chemical and corrosion resistance upon exposure to ultraviolet light. This objective is to provide epoxy resin with improved physical or mechanical properties by silane coupling agent. In view of the commercial interest shown by the reinforced plastics and adhesion industry, silane coupling agents are in use. Plueddeman et al. [18] reported on the use of mixed silane coupling agents in primers and coupling agents for composites. The benefit is to derive this coating by using mixed silanes rather than single silane coupling agents. In this work, free-radical curing matrix polymers benefit least from mixed silanes on the reinforcement. Single reactive silanes with methacrylate or styrene functionality react completely in a free-radical initiated polymerization. Dilution with an amino-functional silane may be beneficial in condensing the siloxane with an inorganic substrate. High temperature composites benefit the most if stable aromatic silanes are mixed with organofunctional silane in the coupling agent. Foscante et al. [19] reported on the epoxy-based coating material with improved solvent, acid and base resistance by forming an interpenetrating polymer network (IPN) of polymerized epoxy resin network intertwined with a polysiloxane network formed by the hydrolytic polycondensation of silane groups. A preferred method for preparing the IPN is to react the epoxy resin with aminosilane and silicone intermediate resin capable of both hydrolytic polycondensation of the silane moiety and amine addition of the oxirane rings of the epoxy resin. The selection of solvents affects the relative rates of reaction. Hydrocarbon solvents, which have no affinity for water, have little effect beyond increasing monomer mobility and reducing the monomer concentration. Alcohol solvents best catalyze the epoxy-amine reaction, but also absorb water from the atmosphere to facilitate the distribution and availability of water for condensation of silane groups. A more complex situation arises when ketone solvents are used. Ketones react reversibly with primary amines to form ketimines and water, also the hydrolysis of silane by the water from ketimine formation accelerates the formation of

the polysiloxane portion of the IPN. Thus, the interpenetrating polymeric matrices are comprised of intertwined epoxy-polyamine and polysiloxane network, which resulting structure has physical and chemical properties much improved over those of either polymeric component alone. Witucki et al. [12] studied on the application of alkoxy silanes for use as adhesion promoters, crosslinkers and hydrophobes. The basic methods of utilizing silanes in a coating application are (1) Surface treatment, which treatment is formulated into primers by applying silane from aqueous alcohol solution. The solution can be wiped, dipped or sprayed onto the surface. (2) Additives into paints, inks and adhesives; the silane becomes a component of the coating from which it diffused or migrated to the inorganic substrate and reacts. (3) Reactive intermediate for silicone resin synthesis and organic resin modification, such as alkoxy silanes, when cold blended with acrylic emulsion. These silicon acrylic emulsions have shown to have improved weathering characteristics. By utilizing a unique blend of methoxy silanes, a silicone modified latex improved the gloss retention and color retention. Each of these methods requires special consideration. Kim et al. [20] studied various silane-modified poly(vinyl imidazole)s synthesized, and the corrosion protection for copper at elevated temperature and in humid condition. Vinyl imidazole (VI) was copolymerized with four silane coupling agents, namely: allyltrimethoxysilane (ATS), γ -methacryloxypropyltrimethoxysilane(MPS), 3(*N*-styrylmethoxyl-2aminoethylamino) propyltrimethoxysilane hydrochloride (STS), and vinyltrimethoxysilane (VTS), by free-radical copolymerization. All copolymers show good corrosion protection capability, the thermal stability of copolymers depends on the length of the side chain in silane coupling agents. The copolymer with the long side chain Poly(STS-co-VI) has hardly formed the siloxane network structure. Hull et al. [21] developed epoxy coating by synthesis of epoxy-siloxane hybrid polymer, upon exterior exposure, an epoxy coating becomes chalk and lose all of its gloss quickly. Therefore, gloss retention is required, 50 μm of an aliphatic polyurethane top coat must be used. The

free isocyanate groups in urethanes lead to toxicity concerns. Epoxy-siloxane hybrid polymers have weathering and physical properties greatly exceeding those of both a typical epoxy and an aliphatic polyurethane. Turner et al. [22] studied the work dealing with characterization of 3-(trimethoxysilyl)propylmethacrylate (γ -MPS) grafted onto ZrO_2 powder surface. The modified ZrO_2 powder was studied using x-ray photoelectron spectroscopy (XPS), FTIR and NMR. The proposed model suggests bonding of the γ -MPS molecules to the ZrO_2 powder surface through Zr-O-Si bonding, accompanied by interlinkage between individual γ -MPS molecules via Si-O-Si bonding. The described bonding configuration may also be applicable to other ceramic oxide-organic silane molecule-modified systems, particularly for the case of TiO_2 . Quinton et al. [23] investigated of organosilane adsorption mechanisms through the use of a model adsorbate and substrate system. Propyltrimethoxy silane (PTMS) is suited to the study of the silane surface bonding mechanism. The ability of metal oxide surface to form an interfacial bond with silane coupling agent is related to the electrokinetic character of the surface. The greatest silane adsorption is expected to occur on surface with the lowest values of the isoelectric point (IEP). Quinton et al. [24] investigated the structure of γ -aminopropyltriethoxysilane (γ -APS) on mechanically polished iron oxide surface. The situation for hydrolyzed γ -APS, which molecule possesses two moieties on aminopropyl group and silanol species, that interact with an oxide surface. The γ -APS molecule is capable of bonding to the oxide surface via both the silanol and amine groups. The preferred bonding group, and hence the orientation of the molecules, depend upon the isoelectric point at surface and the solution onto iron substrates at pH 10.4. The deposited films possessed a significant fraction of molecules bonded to the surface through protonated amine groups. A model of the possible adsorption conformations is displayed, three possibilities for molecule orientation on the surface. The conformation of type (a) molecule is adsorbed via a protonated amine group and an amine group at the surface/film interface. Type (b) corresponds to the

possibility where each end of the molecules may be bonded to the surface, and type (c) the molecule is bonded through silanol adsorption and condensation to form Si-O-Si metallosiloxane bonds. It is conceivable that all three conformations exist on the surface. The relative concentrations of protonated amine-surface bonding varies with time. Jang et al. [25] studied and analyzed the epoxy/silane coating steel system at elevated temperature and in humid conditions. They also investigated types of silane coupling agents to epoxy for steel corrosion protection. Silane coupling agents of *N*- β -aminoethyl aminopropyltrimethoxysilane (AAPS), γ -glycidoxypropyltrimethoxysilane (GPS) and bis[3-(trimethoxysilyl)-1-phenylpropyl]tetrasulfide (RC-2) were introduced as primers into an epoxy/steel system. Aminoalkyl-functional silane (AAPS) inherits higher corrosion protection capability than glycidoxy (epoxy) functional methoxy silane (GPS) and trimethoxysilyl (sulfide) functional silane (RC-2), because aminoalkyl-functional silane (AAPS) has an amine functional group that can act as a catalyst for hydrolysis and condensation to form siloxane network, which is thermally stable at elevated temperatures and resistant to water diffusion into the interface between the coating material and steel.