EFFECT OF SILANE ON VISCOELASTIC BEHAVIOR OF EPOXY UNDER HYGROTHERMAL CONDITIONS

By

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This study examines impact of (3 – Glycidyloxypropyl) trimethoxysilane coupling agent on epoxy resin by matrix modification. Different weight percentages of silane were added to neat resin to investigate how silane's reaction with epoxy changes important properties of the material before and after moisture absorption. Nanoindentation was employed to evaluate mechanical properties taking into account viscoelastic nature of the material being studied. Water degradation of samples were conducted both at room temperature and 50 ℃ to gain insight into changes caused by absorption of water and effect of increase in temperature. It was observed that silane degraded various properties of neat resin such as elastic modulus, hardness and creep resistance. Differential scanning calorimetry (DSC) results indicated that glass transition temperature (T_g) of the material was also lowered. However, the most interesting observation was that for 2 wt. % silane samples which were subjected to 50 ℃ water degradation there was increase in creep resistance as well as glass transition temperature. Fourier transform infrared spectrospcopy (FTIR) was used to analyze chemcial interaction which could have been attributed as the reason behind possible increase in cross linking of epoxy under sub boiling water degradation environment.

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CHAPTER I

INTRODUCTION

Last few decades of 20th century have witnessed rapid progress in research of fiber reinforced composites for supporting a spectrum of applications in industries that constitute the backbone of the world economy. The potential of fiber-reinforced composites are highly dependent on its components like matrix and fiber. The interface between fiber and matrix has provided a very interesting space for researchers around the globe to study and over the years it has resulted in more efficient material properties by enhancing the bonding between the constituents [1, 2].

The primary objective of developing advanced high performance materials is to obtain materials with high modulus and strength. In this pursuit, many problems are being encountered such as sudden decline in interface bonding on an extended spell of exposure to humid and cycle of severe temperature fluctuations. Many methodologies are being tried to ameliorate the effect of environmental conditions on mechanical properties of these materials [3]. Generally these methods that are used to enhance the interfacial adhesion between fiber and matrix can be classified into two categories: altering matrix properties method and treating the fiber surface. The latter method includes sizing which involves changing the nature of the fiber surface [4]. Matrix modification aims at increasing toughness of matrix and promoting the creation of reactive sites of significant chemical affinity towards fiber. Addition of coupling agents which generally composes of an organic and inorganic group into the matrix is a very common matrix modification method. It will be interesting to explore about impact of adding silane coupling agent into epoxy resin.

1.1 Epoxy polymers

Epoxy polymers form an advanced class of materials due to their densely cross-linked molecular structure. This has enabled epoxies to possess many attractive mechanical and thermal properties like high modulus and strength, high creep resistance, high glass transition temperature (T_g), low shrinkage and so on. They reach their maximum potential in terms of mechanical properties when they are fully cured or in other words completely cross-linked in the structure in which they are present. The biggest interest in epoxy resins system is from the fact that there are wide variety of materials and chemical methods to cure them and thereby providing a broad list of appealing properties. Curing agents and catalysts may also be introduced to the system to improve the rate of curing of epoxy resins. The ease of manufacture makes them desirable for applications in automotive, aerospace and packaging industries. Among numerous applications, the most notable one involves their use as matrix for fiber reinforced composites.

Different types of micro and nanoscale fillers like clay particles [5], alumina particles [6], polyhedral oligomer silsesquioxanes (POSS) [7, 8] and carbon nanotubes [9] have been examined to enhance the mechanical properties of epoxy polymers. Exposure of epoxies and epoxy composites to moisture, variation in temperature, UV radiations and other adverse environments are common as a part of their application [10]. Many studies conducted over the years have explained about undesired impact of these harsh environmental conditions on the exceptional mechanical and thermal properties exhibited by epoxies [11, 12, 13, 14].

Epoxy polymers are hydrophilic in nature which implies that they have high affinity toward water content or high moisture absorption tendency. Studies by Soles *et al.* have revealed that structures based on epoxy resins are prone to high moisture absorption and the range of equilibrium moisture uptake can vary from 1 to 7% [15]. Different modes of water absorption in these systems was discussed by Apicella *et al.*[16] that involves bulk dissolution of water into network of polymer and also by hydrogen bonding between hydrophilic groups of polymer and water. It has been found that absorbed moisture generally tends to degrade their mechanical properties by altering their physical and chemical characteristics. Several mechanisms are behind this change such as plasticization, crazing, hydrolysis etc. While most of the mechanisms are irreversible, it is considered that upon drying effects of plasticization can be reversed. Studies have revealed that there was decrease in modulus of epoxy after moisture absorption [17]. Published works have shown that degradation of mechanical properties can be considered as an amalgamated effect of high temperature and moisture [18].

Epoxy resins have also been accepted widely in making of protective coatings due to their very strong adhesive and chemical resistance properties along with their superior processing attributes. Preiswerk and Gams were the first to identify the exceptional adhesive properties of epoxy resins in 1944 [19]. But it is important to realize their inability to behave well in humid environments. It has been noted in different studies that there was notable amount of water absorption in their system that lead to degradation of their highly preferred characteristics. Some researchers have indicated saturated water content in coatings made of epoxy resins can be significantly up to 10% [25]. Different approaches including pretreatment based on forming of films are being tried to improve the response of epoxy coatings to the harsh environmental parameters they are being exposed.

Use of coupling agents to improve interfacial adhesiveness are gaining lot of interest among researchers. Hydroxyl-terminated polybutadiene was used to modify epoxy matrix to improve mechanical properties of short carbon fiber-reinforced epoxy nanocomposites [20]. Jannerfeldt *et al.* explored the impact of matrix modification on the interfacial strength and mechanical performance of polypropylene glass fiber reinforced composites [21]. Silane coupling agent commonly used for fiber-surface sizing are also being tried for matrix modification. However, studies involving silane coupling agent in matrix modification are inadequate.

1.2 Silane coupling agent

Silanes are identified as effective coupling agents widely employed in composites and adhesive systems. Researchers have been successful using them in inorganic filler reinforced polymer composites like glass fiber reinforced polymer composites. Xie *et al.* has provided a complete review of the progress in using silane coupling agent for manufacturing of fiber reinforced polymer composites [22]. Silanes have also found use as adhesion enhancers in adhesive systems due to their exceptional ability to provide strong adhesion.

Silane coupling agents are silicon based chemicals with both inorganic and organic reactivity present in the same molecule. The generic chemical structure of silane coupling agent is given by equation 1.1 [22].

$$R_{(4-n)} - Si - (R'X)_n \; (n = 1{,}2) \tag{1.1}$$

Here R is an alkoxy group, X refers to organofunctionality and R' is the alkyl bridge connecting organofunctionality and silicon atom. The compatibility of the organofunctional group with polymer matrix is very vital for the interaction between the two. Organofunctionalities of silanes generally include amino, vinyl, mercapto, methacryloxy and glycidoxy groups. Functionally silane as coupling agent may be used as a surface modifier, a sizing agent or as an adhesive material based on the bonding material's thickness along the interface [23]. Generally they are used to act as an interface to bond between organic material and inorganic substrate.

Silane has found use in fiber treatment to increase bonding with the matrix and has proved their capability in reducing moisture uptake in fibers under humid conditions [24]. Their use are quite significant when water attacks interface between reinforcement and matrix and weakens or destroys the bond between the two. Silane coupling agents have shown ability to increase the bond strength and also avoid de-bonding along the interface as a result of composite aging [22].

Use of silane as coupling agent with epoxy coating was also studied by some researchers. Ji *et al.* found that water absorption can be reduced in epoxy coatings by incorporating silane monomer. It was noted that the glass transition temperature (T_g) of silane – epoxy coating increased continuously during immersion in water which is generally not seen in silane free polymeric substrates and also tends to decrease considerably after water absorption [25]. Recent researches discusses about improvement in corrosion resistance of epoxy coating by addition of silane [26].

It is essential for silane molecule to have bifunctional groups that will react with the two components of composites in order to develop a bridge between them and thereby provide an effectual coupling between fiber and polymer matrix. For epoxy as target matrix, researchers commonly use silanes with functionalities such as amino or glycidoxy.

Hydrolysis of silane forms an interesting string of reactions that results in formation of bonds which provide the desired characteristics. It is generally a 4 tier process involving hydrolysis, condensation, hydrogen bonding and bond formation. Usually organo-silanes are composed of an organic substituent and tripartite hydrolysable alternate.

In most of the cases hydrolysis is marked by formation of entities containing silanols. It is a functional group with connection $Si - O - H$. The first step involves hydrolysis of the three reactive OCH_3 groups attached to Si and results in 3 parts of methanol (CH_3OH). Next step is condensation to a polymer with comparatively few number of repeating units known as oligomers. The OH group present in the substrate offers the option to form hydrogen bond by the oligomers. The last step is associated with loss of water in formation of covalent bonding with the substrate generally during curing.

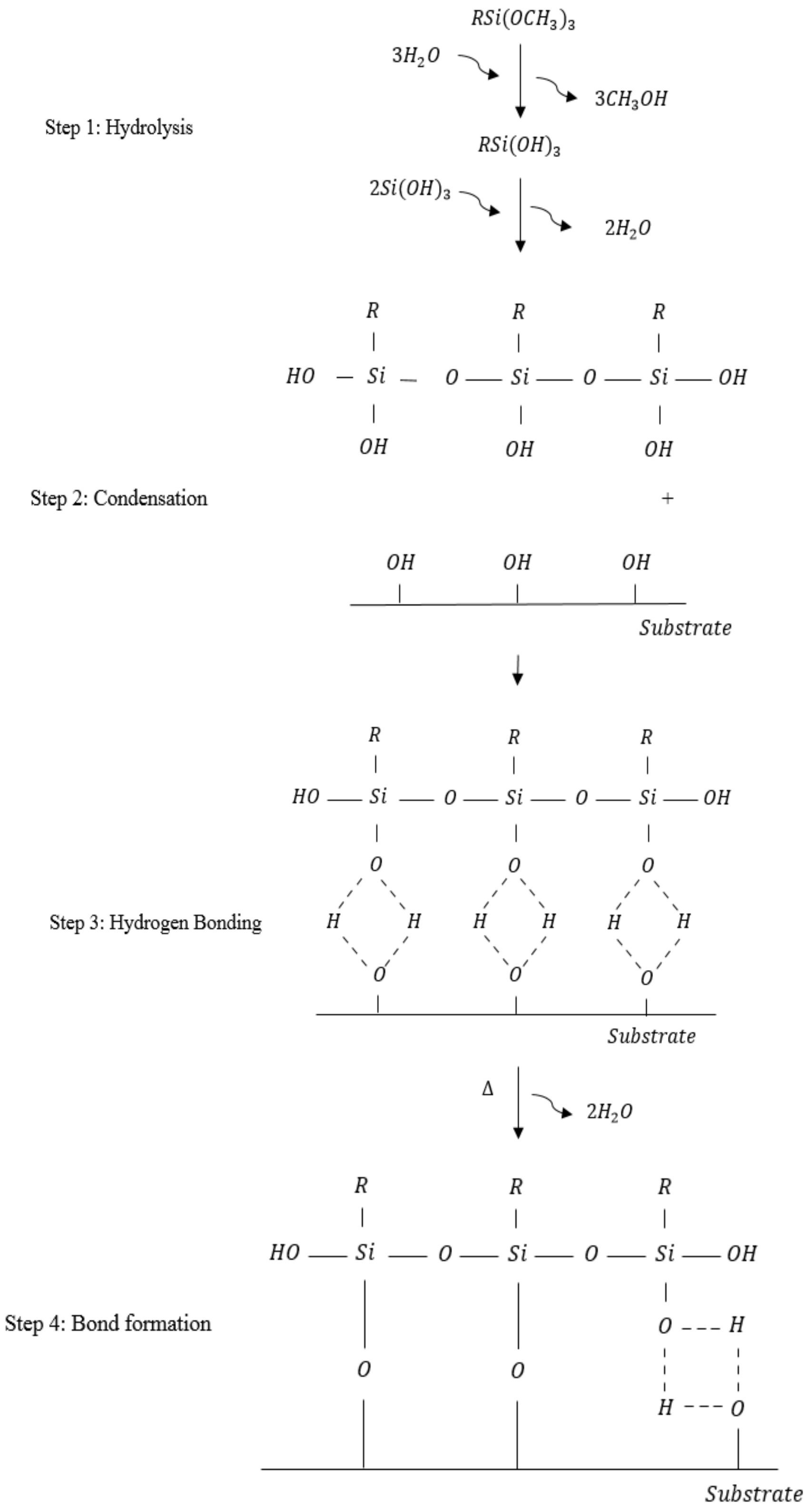

FIGURE 1.1 Hydrolysis of silane (adapted from [27]).

The four steps involved in the hydrolysis of silane coupling agent in general takes place concurrently after the initiation of the first step. Along the boundary between substrate and organo-silane there is one bond from each Si present in organo-silane to the surface of substrate material. The other two groups of $Si - O - H$ are usually in condensed form or free in nature. The $R'X$ group of the organo-silane is accessible for covalent bond formation or any other physical form of interaction in other stages [27].

It is good to note that water needed for hydrolysis of organo-silane may be available in many forms. It can be by direct addition of water or water content existing on substrate or it can even be from moisture content present in atmosphere. The organic substituent and amount of water accessible for hydrolysis will determine degree of polymerization of the organo-silane. It is important to understand that covalent bond formed with the substrate during hydrolysis are generally reversible in nature and during curing for few hours when water content is being removed these bonds can form, break or reform to alleviate internal stress [27].

Silanes can connect with substrate under dry conditions or moisture free environment. The reactive OCH_3 group joins with OH group present in the substrate to release methanol and thereby form bond with the substrate. Methoxysilanes are considered most effectual in forming bond with substrate under these environmental conditions.

1.3 Nanoindentation and measurement of mechanical properties

Indentation testing involves bringing in contact a material of unknown mechanical properties with a material of known properties and thereby ascertain properties such as Young's modulus and hardness of the material of interest [28]. Most of the hardness tests like Brinell, Knoop and Vickers have the penetration length scale in 10^{-3} m range. When the length scale of penetration is in 10^{-9} m range, the indentation test is known as nanoindentation. Forces used in nanoindentation are in milli-Newtons (10^{-3} N) range and its resolution in few nano-Newtons. As measurement of properties are now possible in micrometer and nanometer scales, it is possible to determine properties of very thin films and small structural features [29].

It is useful to realize the difference of nanoindentation from other indentation tests. An important feature of nanoindentation is the indirect measurement of area of contact between specimen and indenter. Direct measurements are used in conventional indentation tests that is by measuring the features of impression left after indentation. Using direct measurements in nanoindentation is not viable. So experts have developed a method to use depth of penetration and known geometric features of indenter to determine the contact area at full load condition. This method of testing has found use in determination of elastic modulus, viscoelastic properties and fracture toughness in case of brittle materials.

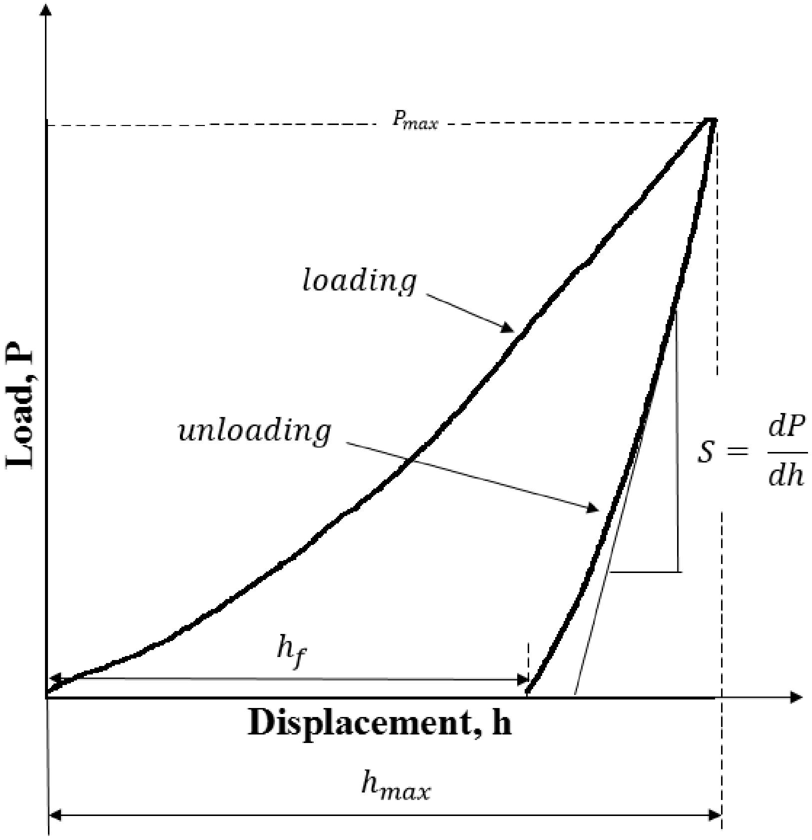

FIGURE 1.2 Load – Displacement curve obtained from nanoindentation test.

Fig 1.2 is obtained when an indenter is in contact with the surface of a material of interest that is flat with steady increase in load applied. For each increment in load, the penetration and load values are recorded. After the maximum load is reached based on the load function, unloading takes place at specified rate. Load and depth of penetration data are recorded during unloading too. The loading part is marked by initial elastic contact and then plastic flow or yield at larger values of load. If yield occurs anywhere during load history, a different path is traced by load – displacement curve till load becomes zero. The slope of unloading curve at the tangent to point of maximum load and maximum depth of indentation at a specific load can be used to infer Young's modulus and hardness of the specimen under consideration.

There are some viscoelastic materials such as epoxy where indentation tests will be characterized by effect of creep that is there will be an increase in indentation depth on application of constant load as shown by the hold region in Fig 1.3.

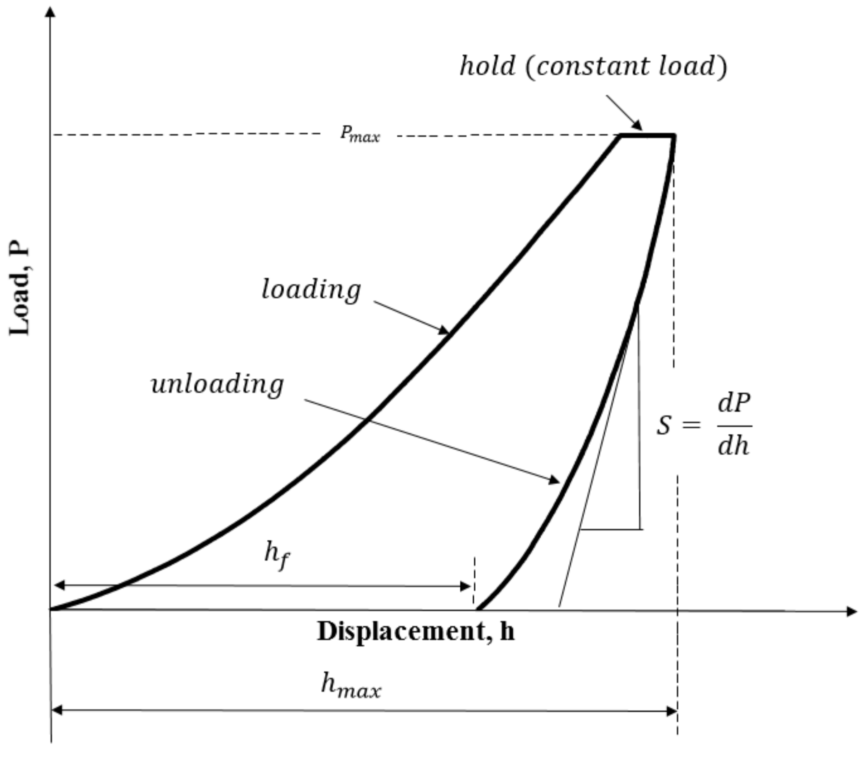

FIGURE 1.3 Load – Displacement curve with hold region.

Analysis of the creep portion will be useful to gain insight into viscous nature of materials. Based on load function of nanoindentation, we can find creep compliance or relaxation modulus of viscoelastic materials.

In 1986, Doerner and Nix proposed a method to use data from depth sensing tests to evaluate properties like hardness and elastic modulus. They used flat punch approximation and unloading curve was linear as contact area remained constant during withdrawal of the indenter [30]. Oliver and Pharr in 1992 extended the work to incorporate for unloading curves that are markedly curved when conical and spherical indenters are used as contact area is not constant [31].

It was identified that there are three parameters that must be determined from load-displacement ($P - h$) curves to evaluate useful mechanical properties of the material of interest. It includes, maximum load (P_{max}), maximum depth of indent (h_{max}) and contact stiffness ($S = dP/dh$) that is the slope of unloading curve in its initial stages.

A fully developed plastic condition is used as criteria to determine hardness of a material by indentation method. The reason behind this is that in fully developed plastic zone the mean contact pressure is usually non-dependent on load and only material response acts as a factor. Meyer hardness which relates to mean contact pressure (P) at full load which is P_{max} over projected area of contact (A) is generally used to evaluate hardness for nanoindentation testing.

$$H = \frac{P_{max}}{A} \tag{2.2}$$

Fig 1.4 shows a schematic sketch of unloading process along with parameters that are used to describe the contact geometry.

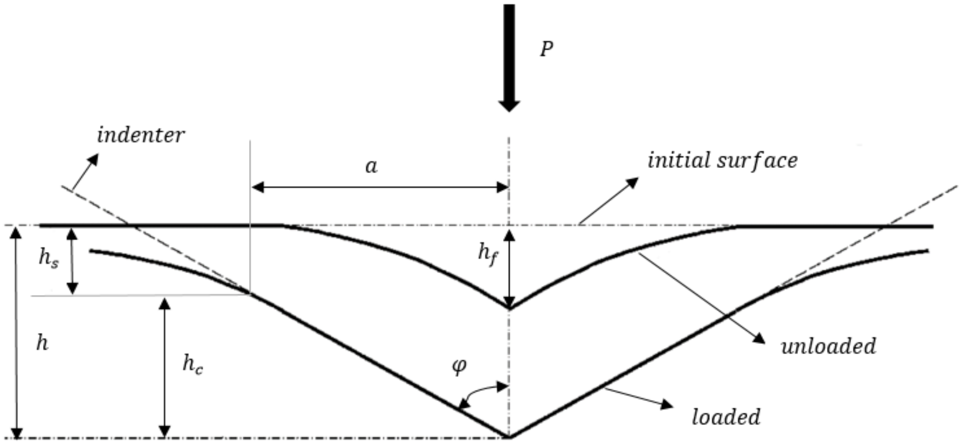

FIGURE 1.4 Schematic sketch of unloading process (adapted from [29]).

Depth along which contact is made between specimen and indenter, h_c is given by the relation:

$$h_c = h_{max} - h_s = h_{max} - \epsilon \frac{P_{max}}{S} \tag{3.3}$$

Determination of A, area function which is also known as indenter shape function is done by independent measurement taking into consideration the changes in tip geometry from the ideal condition. It is generally expressed as a function of depth along which contact is made between specimen and indenter which is given by h_c.

$$A = F(h_c) \tag{4.4}$$

Researchers have found using finite element simulation that the standard value of ϵ to be 0.75. It is considered as a good estimate to be used along with experimental data [29]. Relationship between contact area, elastic modulus and measured unloading stiffness is used in evaluation of unknown elastic modulus of given material.

$$S = \beta \frac{2}{\sqrt{\pi}} E_{eff}\sqrt{A} \tag{5.5}$$

Here β is a constant that takes in to consideration the change in stiffness due to shortage of axial symmetry for indenters like Berkovich that are pyramidal in shape. E_{eff} is the effective modulus that takes accounts for the elastic displacements that occur in specimen with elastic modulus E and Poisson's ratio υ and indenter elastic modulus and Poisson's ratio denoted as E_i and υ_i respectively.

$$\frac{1}{E_{eff}} = \frac{1 - \nu^2}{E} + \frac{1 - {\nu_i}^2}{E_i} \tag{6.6}$$

Initially this expression was derived for elastic contacts alone, but subsequent studies have shown that it is applicable to elastic – plastic contacts as well. It has been also noted that the above equation is not influenced by pile-up and sink-in [32].

1.4 Objective

There are lot of researches that have investigated fiber surface treatment techniques to improve interfacial adhesiveness. Recently matrix modification using different coupling agents are also being explored for the same reason. Silane as mentioned previously has great potential to be used as coupling agent along with epoxy. Yang *et al.* explored addition of amino based silane on epoxy matrix [33]. It was reported that there was increase in flexural strength when epoxy resin was modified with silane having amino functional group. (3 – Glycidyloxypropyl) trimethoxysilane has glycidyloxy group attached which is compatible with epoxy. As discussed previously, methoxysilanes are very effective in forming bond with substrate under unhydrous conditions. As it is a widely used form of silane coupling agent, it was selected to modify neat epoxy resin in this study. Recently Sandeep had conducted a study about influence of (3 – Glycidyloxypropyl) trimethoxysilane on mechanical properties of epoxy [34]. It was noted that properties of epoxy degraded upon modification by silane. There was an improvement in mechanical properties of modified resin under hygrothermal conditions. The viscoelastic behavior of epoxy was ignored in the study and therefore the values of elastic modulus and hardness that were obtained are not accurate. In this study epoxy was assumed to exhibit linear viscoelasticity to obtain accurate values of elastic modulus and hardness for modified epoxy. Effect of (3 – Glycidyloxypropyl) trimethoxysilane on viscoelastic behavior of epoxy have not been investigated thus far. So it seemed interesting to understand how addition of silane influenced creep behavior of viscoelastic material like epoxy. In this study, room temperature and sub-boiling temperature water degradation are used to explore how creep behavior of modified epoxy was affected under hygrothermal conditions.

Silane was directly incorporated at different wt. percentages to epoxy resin with the aim to explore effect of increasing wt. percentage of coupling agent on neat resin. Nanoindentation technique was employed to evaluate mechanical properties such as elastic modulus and hardness taking into account viscoelastic nature of epoxy. Variations in glass transition temperatures of all samples are considered to provide insight into how silane coupling agent behaves with epoxy resin. Spectrographic methods like Fourier transform infrared spectroscopy (FTIR) are employed to examine the chemical changes in each type of sample and to understand the underlying chemical interactions that may be causing the mechanical properties and viscoelastic behavior of epoxy to change.

CHAPTER II

MATERIALS AND METHODOLOGY

2.1 Materials

The epoxy resin used in this work was diglycidyl ether of bisphenol F designated by supplier as EPON 862 (made by Miller-Stephenson Chemical Company, Dunbury, Connecticut, USA). Its density is 1.17 g/ml. It is a low viscous liquid resin made from epichlorohydrin and Bisphenol – F. A moderately reactive, low color and low viscous aliphatic amine with a gel time of 135 minutes was used as the curing agent (EPIKURE 3274 made by Miller-Stephenson Chemical Company, Dunbury, Connecticut, USA). Density of EPIKURE 3274 is 0.952 g/ml.

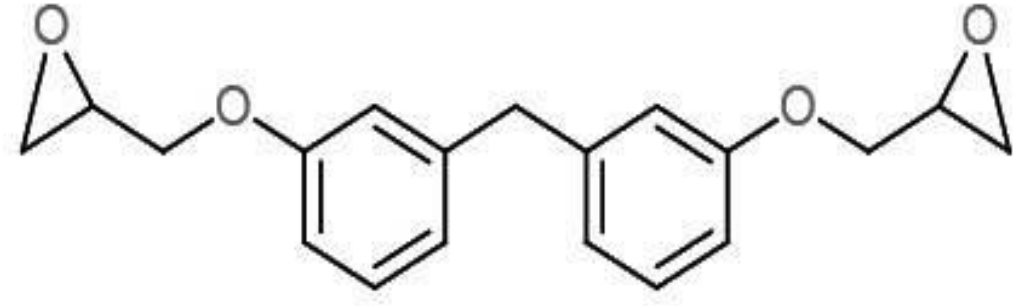

FIGURE 2.1 Chemical structure of EPON 862

(3 – Glycidyloxypropyl) trimethoxysilane which is commonly abbreviated as GPTMS was used as the coupling agent and had an assay greater than 98% (made by Sigma-Aldrich Corp., St. Louis, Missouri, USA). Its empirical formula is $C_9H_{20}O_5Si$ and has a molecular weight of 236.34. Its density is 1.07 g/ml. GPTMS is one of the most commonly used form of silane coupling agent and presence of glycidyloxy organofunctional group in the silane makes it more compatiable with epoxy. GPTMS was selected for this study as methoxysilanes are reported to be more effective in forming bonds with substrate even under absence of water.

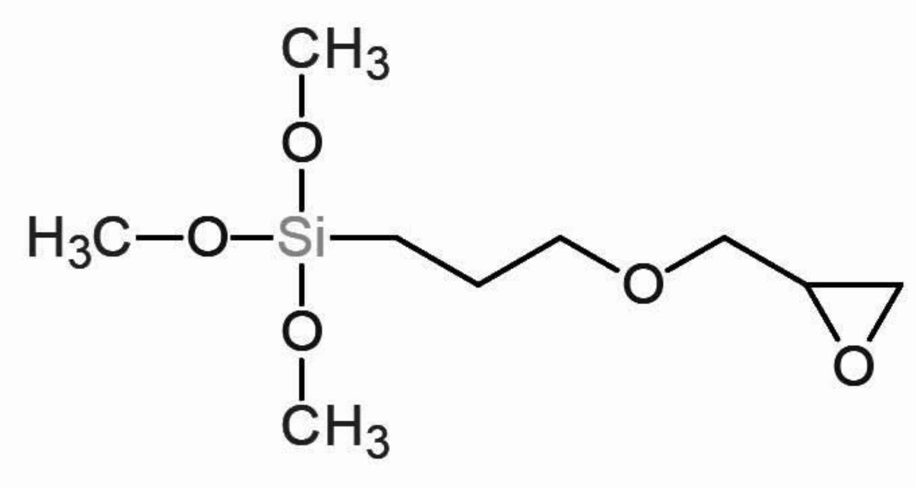

FIGURE 2.2 Chemical structure of GPTMS

2.2 Sample preparation

All samples in this study were made under normal room conditions. The quantities of EPON 862, EPIKURE 3274 and GPTMS that had to be used was determined such that EPON 862 and curing agent EPIKURE 3274 are mixed in the ratio 100:40 by weight. GPTMS was added in different net weight percentages ranging from 0% to 2% to determine influence of increasing quantity of silane on cross linking of epoxy resin and to understand the ideal amount of silane needed to improve properties of epoxy. The densities of each material was used in computing quantities of each to be added in the sample.

Epoxy resin and silane according to quantity determined earlier was mixed slowly for 5 minutes and followed by which curing agent EPIKURE 3274 was added to the mixture. Slow hand mixing for about 15 minutes was done to ensure that no air bubbles were being introduced into the mixture. In order to remove any air bubbles that might have been entrapped in the mixture, it was kept for degassing in a vacuum chamber at 26 inches of Hg vacuum twice for periods of 10 minutes each. The air bubbles that rose to the top of the mixture during degassing was skimmed off to obtain mixture free of air bubbles.

Circular molds of 25.4 mm diameter and 25.4 mm thickness (made by Buehler, Illinois, USA) was used to make the samples. Mixtures of different ratios of silane was poured separately into molds to obtain three samples of each type and it was left to cure for 24 hours at room temperature of approximately 25℃. Post curing was carried out for all samples at 121℃ for 6 hours.

The samples were cut using precision cutting machine ISOMET 1000 (made by Buehler, Illinois, USA) at a thickness of 2.5 mm each. Coolant was not used during cutting to ensure there was minimum moisture content for hydrolysis of coupling agent before being exposed to hygrothermal conditions. Cutting of samples were carried out at 100 rpm and load of 50 N using an electroplated nickel bonded thin kerf diamond blade of 127 mm diameter. These types of blades are ideal for use in dry cutting of thermosetting polymers, graphite, soft ferrites and electro carbons. It also requires very less frequency of dressing compared to metallic bonded blades and offers highly precise quick cuts that are free of chips.

Polishing of samples were done using Labopol 5 polisher (made by Struers, Ohio, USA) with an attached automated head named as Laboforce 3. Automation of polishing process ensures consistent loading and uniform direction of polishing. The key aspect in polishing of samples was to achieve an optically clear and relatively flat surface for performing nanoindentation. Samples were polished under dry conditions in order to avoid introduction of moisture content that could result in hydrolysis of coupling agent before water degradation. Polishing was done on one side of the sample using silicon carbide (SiC) grits of 320, 400, 600 and 800 at 100 rpm for two minutes each Final step involved polishing using SiC grit of 1200 at a speed of 250 rpm for one minute. It was carried out at a higher speed to avoid adhesion between sample and SiC grit paper. It produced a surface that was visibly free of any ridges or troughs.

A consistent load of 10 N was applied over each of the three samples placed on specimen mover plate. It was necessary to ensure all samples are relatively flat in order to perform nanoindentation on it. Hence surface opposite to the polished side of all samples were hand polished quickly using SiC papers of grit size 320. Using a circular spirit level, flatness of all samples were checked and confirmed.

Each sample's thickness was reduced by polishing such that top and bottom surface area of the sample combined together would be approximately 90% of the curved surface area. It will help to approximate water absorption during water degradation test as one dimensional phenomenon.

2.3 Water degradation of samples

It is essential to explore how change in environmental parameters affects the response of materials under consideration. In this study, one batch of samples comprising of one from each type of sample with silane wt. percentage varying from 0 to 2% was subjected to water degradation at room temperature and another batch of samples were water degraded at sub boiling temperature of 50 ℃. All samples were weighed and their thickness measured before being subjected to water degradation. Distilled water was used for water degradation in order to avoid the influence of any impurities present in water on hydrolysis of coupling agent and reaction of silane with epoxy. The first batch of samples were kept in an open beaker exposed to room temperature of 21 ℃. The degradation process was allowed to continue for a duration of 48 hours. Initially at intervals of 4 hours and then 8 hours, the weight of neat resin sample and 2 wt. % silane samples were measured.

The intermediate percentages of 0.5 wt. % and 1 wt. % silane samples were measured only at beginning and end of the test. Relative water gain percentage was determined using equation 2.1, where $w(t)$ denotes weight at any given time t and w_{dry} denotes weight of dry sample.

$$Relative\ water\ gain\ percentage = \frac{w(t) - w_{dry}}{w_{dry}} \times 100 \tag{2.1}$$

Similar to room temperature water degradation test, sample weights and thickness were noted at the beginning of the 50 ℃ sub boiling water degradation. Unlike the previous setup for water degradation at room temperature, in this test a heater was used to maintain temperature of water. Distilled water taken in a conical flask was kept in an open beaker of silicon oil bath. Silicon oil ensures uniform heating and thereby minimizing temperature gradients in water. After heater was turned on, it was necessary to ensure water at uniform and stable temperature of 50 ℃ was achieved so that all samples are exposed to similar parameters.

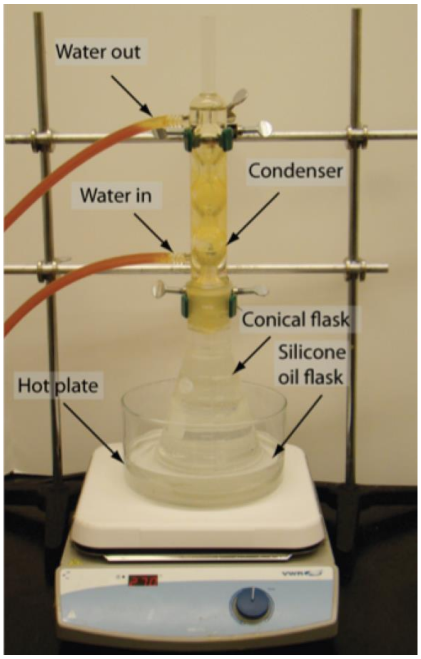

FIGURE 2.3 Sub-boiling water degradation set up [35]

A condenser was used to trap water which evaporated and condense it back into flask so that amount of water in the flask remained constant. The samples were held in the flask using strings in order to allow impact of water on both surfaces of sample. As discussed previously, the thickness of samples had been determined such that one dimensional water absorption can be assumed for both water degradation tests. Weights of samples through 48 hours duration were recorded at pre-determined intervals and at the end of the test using weighing scale with resolution of 0.0001g.

After the test was completed, samples were placed in air tight bags to preserve the condition of the sample. Each sample that was subjected to water degradation was used to perform nanoindentation test in order to determine how mechanical properties like elastic modulus and hardness are influenced under changed environmental conditions.

2.4 Nanoindentation of silane modified epoxy

In this study, nanoindentation was used to determine mechanical properties such as Young's modulus and hardness. Data obtained from the tests are also employed to understand viscoelastic properties of these materials. An MTS Nano Indenter XP system (MTS, Eden Prairie, MN, USA) was used to perform all nanoindentation tests. It has ability to perform nanoindentation up to depths of 500 μm and apply maximum load of 500 mN.

Berkovich indenter which is a three sided pyramidal tip made of diamond was used for performing nanoindentation on all samples. It was assumed that Berkovich indenter can be modeled as an axisymmetric conical indenter with half cone angle of 70.3° which implies that α has a value of 19.7°. The contact area specified in nm^2 and indentation depth given in nm for a Berkovich tip are described often by following polynomial function.

$$A = 24.37\, h^2 + 197\, h - 675.3\, h^{0.5} \tag{2.2}$$

The maximum error for area-depth relation from above polynomial function and modeled axisymmetric conical indenter was reported to be less than 3%. [29]

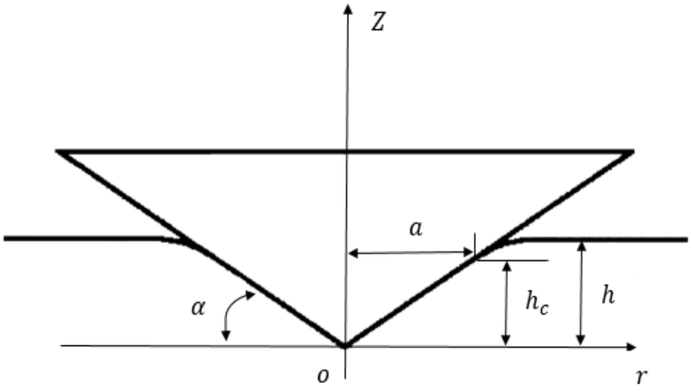

FIGURE 2.4 Geometry of Berkovich tip (adapted from [29])

Samples were placed in the thermally insulated chamber of the MTS Nano Indenter XP system so that it reaches a thermal equilibrium state as that of the indenter and to ensure minimal influence of temperature gradients of testing apparatus on the test conducted.

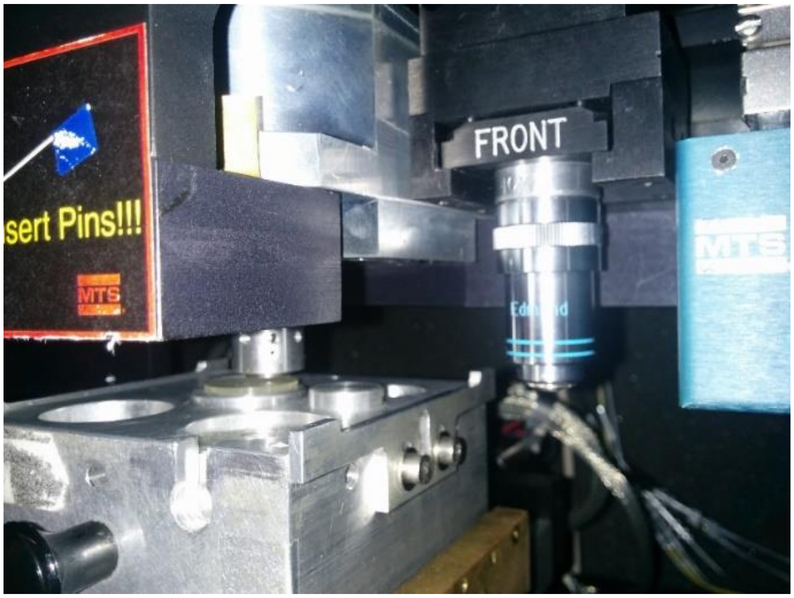

FIGURE 2.5 Sample and testing apparatus of Nano indenter system

In this study load controlled nanoindentation test was performed on all samples to find its mechanical properties. Ramp loading and unloading along with a hold region of constant load as shown in load function given below was used for testing of all samples.

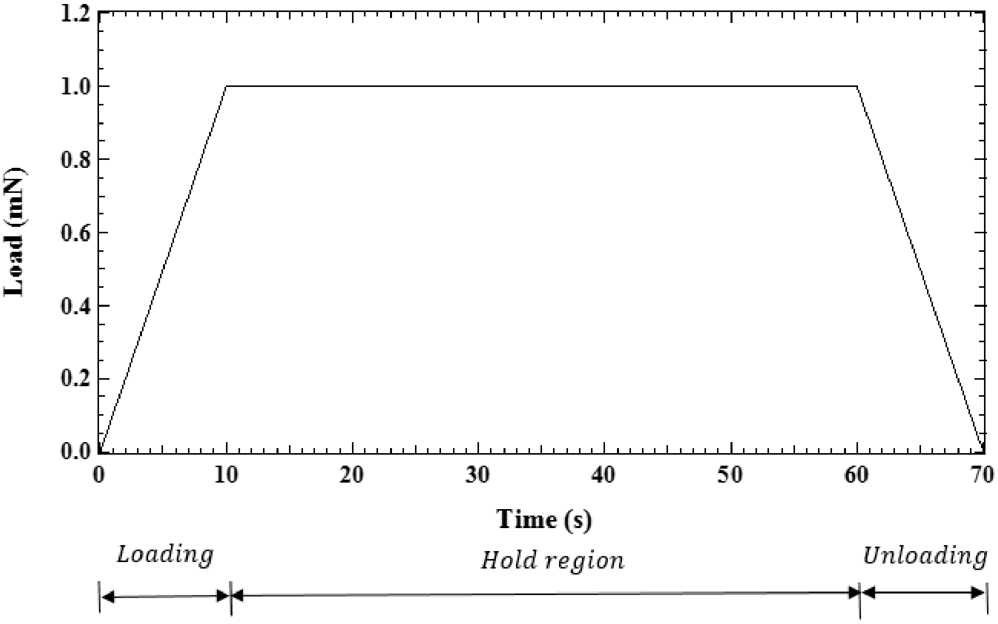

FIGURE 2.6 Load function

Loading was done at a rate of 0.1 mN/s to a maximum load of 1 mN. Thereafter a constant load of 1 mN was applied for a period of 50 s. This is generally referred to as hold region. Full unloading was done at same rate as that of loading that is 0.1 mN/s. Hold region seen in load function is a significant portion of nanoindentation which will be useful to extract information regarding creep and shed more light on viscoelastic behavior of the material being studied. Maximum allowable drift rate was set at 0.15 nm/s to ensure minimum influence on indentation depth data collected during the test. Researchers have found that drift rate is not dependent on the applied load on sample [36, 37].

A square pattern of 4 X 4 was virtually arranged using the Nano Indenter software with a vertical and horizontal spacing of 125 nm between each point. The coordinates of these 16 points was saved by the system and nanoindentation was performed according to the load function at all these points. Each sample was subjected to 16 nanoindentation tests to extract average values of mechanical properties like elastic modulus and hardness. Nanoindentation test on each sample took approximately 180 minutes to complete.

At the end of the test, software attached to the Nano Indenter system provided average value of elastic modulus and hardness of the sample. However, it was very important to note that this result used Oliver Pharr method discussed in previous chapter which was based on the assumption that nanoindentation response during the test can be considered as purely elastic and viscoelastic behavior of the material under study can be ignored. However, for a viscoelastic material like epoxy, the effect of such an assumption on elastic properties can be significantly high.

It has been found that there was an error of nearly 32 % in calculation of elastic modulus when viscoelastic nature of material was not taken into consideration [38]. Feng and Ngan proposed an extension to Oliver Pharr method to incorporate the creep effects while evaluating important mechanical properties like elastic modulus and hardness [38]. Equations 1.3 and 1.5 needed accurate calculation of elastic contact stiffness in order to get true effective stiffness E_{eff}. However it can be easily identified that this stiffness value was apparent and when we consider creep along with elastic deformation, the stiffness will never be same as apparent stiffness S_u.

The relation between true stiffness S and apparent stiffness S_u is given in equation 2.3.

$$\frac{1}{S} = \frac{1}{S_u} + \frac{\dot{h}_h}{|\dot{P}|} \tag{2.3}$$

In the above equation, $\dot{h}_h$ refers to indenter displacement rate at the end of the load hold and $\dot{P}$ is the unloading rate at the beginning of unload.

2.5 Differential Scanning Calorimetry (DSC)

Glass transition temperature (T_g) is an important parameter that can offer insight into how increase in percentage of silane influences cross-linking in epoxy resin. Change in specific heat of the sample during thermal cycle forms the basis for this method. Sizes of samples used are generally very small and are approximately about 10 mg [39].

This test was carried out using Q2000 differential scanning calorimeter (made by TA Instruments, New Castle, DE, USA). Weights of T-zero lid and T-zero pan were measured using a precision scale. A small portion of sample of about 10 mg weight was taken and placed in the pan. The lid was placed on top of the pan and rammed hard to keep the sample in place. The prepared sample was then kept in auto sampler slot. A reference was required during the test so a lid and pan was weighed and rammed together to form reference for samples being tested. The software of DSC apparatus provided the option to perform tests in a sequence. Each sample's weight and its lid-pan system's weight are given as input along with auto sampler slot number in which the sample was kept. Initially sample was equilibrated to -15 ℃ and then subjected to isothermal conditioning for one minute. Temperature was ramped up to 250 ℃ at a rate of 10 ℃$/min$ and again sample was allowed to undergo isothermal process for one minute, which marked the end of cycle 1. It was used to erase previous thermal history of the sample. Cycle 2 involved ramping temperature to -15 ℃ at a rate of 10 ℃/min followed by isothermal process for one minute duration. During cycle 3, the new thermal history of the sample was specified and was used to obtain glass transition temperature (T_g). Here, temperature of sample was increased to 250 ℃ at a rate of 10 ℃$/min$ and then it was subjected to isothermal process for one minute time span.

After all samples are tested, heat flow – temperature plot was obtained depicting thermal history of the sample. The third cycle was used to obtain T_g as we had specified the thermal history of the sample at the beginning of the test.

2.6 Fourier Transform Infrared Spectroscopy (FTIR)

It was essential to understand the chemical interaction that governs the change in behavior and properties of samples based on addition of silane and when subjected to environmental degradation. Fourier transform Infrared Spectroscopy (FTIR) provided an easy and reliable method to generate a spectra of each sample for a range of wavenumbers. FTIR was done using Varian 680-IR spectrometer (made by Agilent Technologies, Santa Clara, CA, USA).

Samples were powdered in order to perform transmittance mode FTIR spectroscopy. Potassium bromide (KBr) was used for providing background to the spectra. 24 scans were used to minimize the influence of noise on the background that was generated. The sample was made by dispersing approximately 5 mg of powdered sample in circa 95 mg of KBr using a pestle and mortar. Sample and KBr used as background was then placed inside the FTIR setup. Laser beam was allowed to focus on KBr and background spectra was collected. Next the focus of laser beam was shifted to the sample dispersed in KBr to generate sample spectra. 24 scans were used in generation of each spectra in order to minimize influence of noise on the spectra as much as possible. The spectra consisted of peaks varying from wavenumbers 4000 cm^{-1} to 400 cm^{-1}. Each peak and wavenumber denoted certain form of bond or element present in the sample. Characteristic IR chart was used to interpret the spectra for each sample. In the spectra obtained, the main regions of interest for study with regard to neat resin and modified epoxy included 3500 cm^{-1} that indicated presence of alcohols, 1650 cm^{-1} which denoted oxidation of cross-linked structure that lead to formation of amides and 910 cm^{-1} that showed stretching of epoxide groups or functionality of epoxy rings [40]

CHAPTER III

RESULTS AND DISCUSSION

3.1 Water absorption profile

Room temperature and sub-boiling temperature water degradation tests were performed on one sample each of silane modified epoxy varying from 0 to 2 wt. % and weight of these samples were mointored at different intervals to understand the rate of water in-take. Figures 3.1 to 3.2 indicate water absorption profile for two temperatures that were used in this study – at room temperature of 21 ℃ and at 50 ℃.

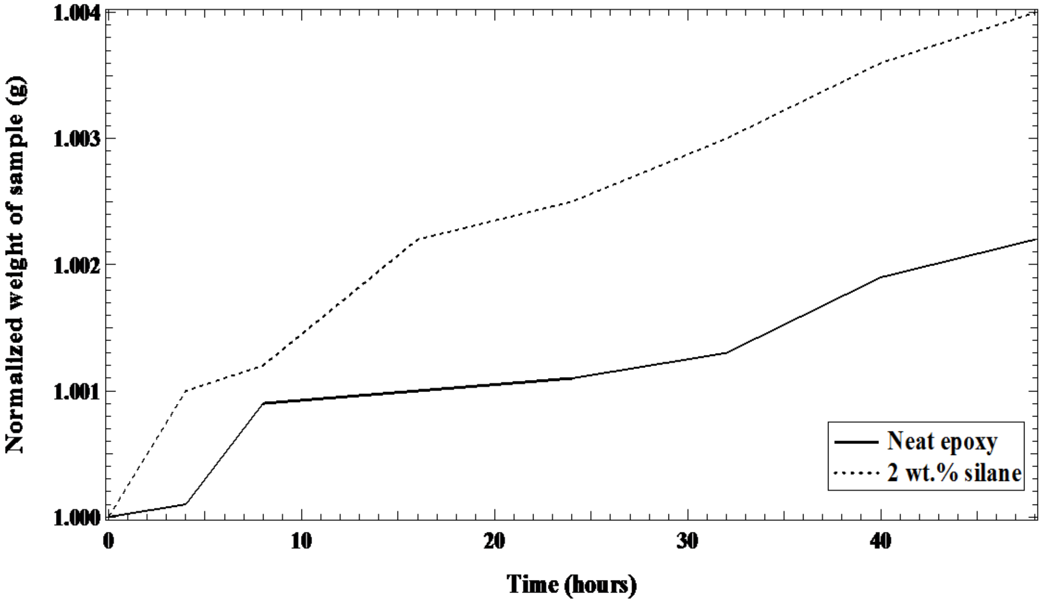

FIGURE 3.1 Water absorption profile of samples at room temperature water degradation

Over 48 hours duration, there was increase in weight of 0.2% for neat resin and 0.5 wt % silane sample. 1 wt. % silane sample showed an increase of 0.3% in its weight. The amount of water absorbed by 2 wt. % silane sample was about twice as that in neat resin. There was increase of 0.5% in the weight of 2 wt. % silane sample. Similar approach was used in [41]. Water degradation test was carried out on all samples at 50 ℃ and Fig 3.2 shows water absorption profile obtained.

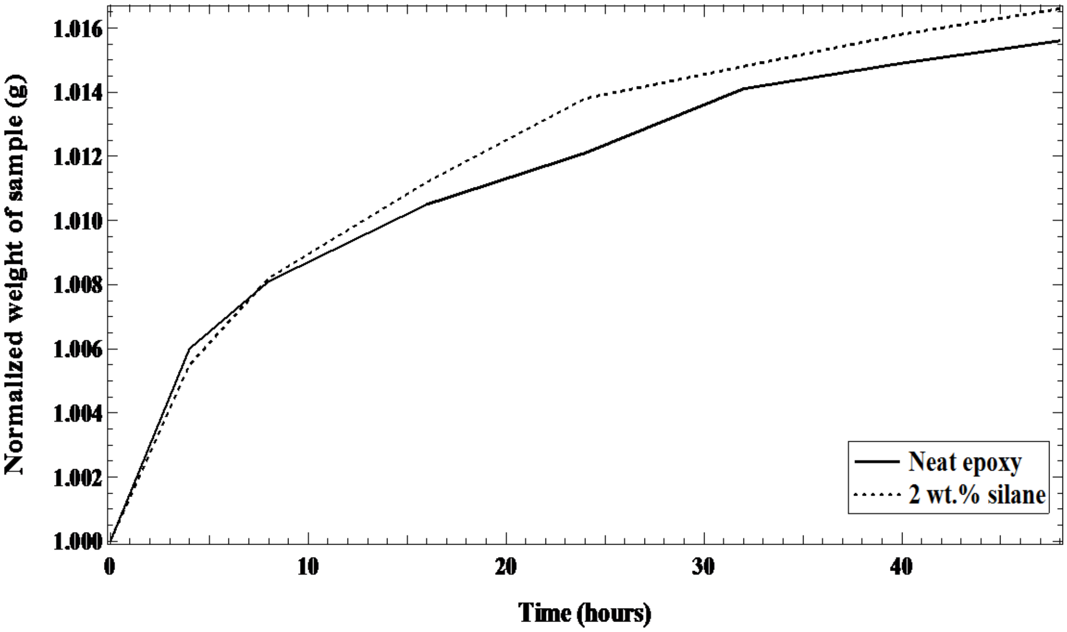

Figure 3.2 Water absorption profile of sample during 50 ℃ water degradation

It can be observed from Fig 3.1 that addition of silane had profound influence on rate of water in-take at room temperature. However at higher temperature the rate of water absorption was comparable for neat and modified epoxy samples. It should be noted that total water gain will not be affected by silane when the samples are subjected to longer periods of water degradation that are close to saturation. During water degradation, the three methoxy groups present in silane monomer absorbs water molecules to release methanol. This leads to formation of silanols in the system which will be key to hydrogen bond forming with epoxy.

3.1 Elastic modulus and hardness

Load – displacement curves obtained using nanoindentation technique described in previous chapter was used to determine vital mechanical properties of material under consideration. Fig. 3.3 shows typical load – displacement curves of the four types of samples in ‘as is’ condition. The initial curve indicates loading, followed by a constant maximum load over hold time of 50 s and third potion of the plot indicates unloading curve.

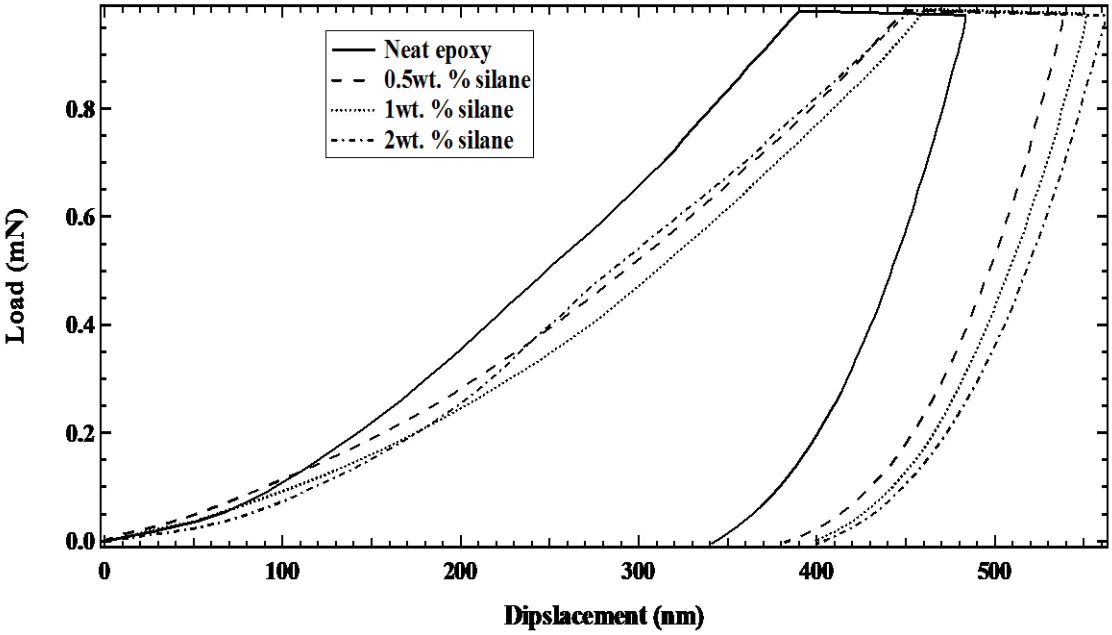

FIGURE 3.3 Nanoindentation load – displacement curves for ‘as is’ condition.

Tables 3.1 to 3.3 shows correction for creep that was used in the load – displacement data obtained from nanoindentation to obtain more accurate values of mechanical properties of modified epoxy. The first goal was to ascertain how addition of silane into neat epoxy impacted its mechanical properties and the second one was to investigate influence of hygrothermal conditions on modified epoxy. Data in first column are values of elastic modulus obtained directly from Nano indenter that was based on Oliver Pharr method. The third column in tables 3.1 to 3.3 indicates reduction in elastic modulus with increased wt. percentage of silane in modified epoxy.

Sample Type	‘As is’ – Elastic Modulus (in GPa)		Reduction in elastic modulus on addition of silane
	Oliver Pharr method	Feng’s creep correction	
Neat epoxy	4.98 ± 0.26	3.36 ± 0.20	-
0.5 wt. % silane	4.65 ± 0.29	3.16 ± 0.24	5.95%
1 wt. % silane	4.31 ± 0.21	3.00 ± 0.25	10.71%
2 wt. % silane	4.25 ± 0.18	2.77 ± 0.16	17.55%

TABLE 3.1 Creep correction for elastic modulus of ‘as is’ samples.

When wt. percentage of silane in modified epoxy was increased, there was degradation of mechanical properties of neat resin. Sandeep had reported decrease in values of elastic modulus for addition of silane up to 1.5 wt. % [34]. Tables 3.2 and 3.3 gives values of elastic modulus for samples subjected to water degradation.

Sample Type	Room temperature water degraded Elastic Modulus (in GPa)		Reduction in elastic modulus on addition of silane
	Oliver Pharr method	Feng’s creep correction	
Neat epoxy	4.45 ± 0.16	2.82 ± 0.17	-
0.5 wt. % silane	4.27 ± 0.17	2.71± 0.17	3.9%
1 wt. % silane	4.24 ± 0.08	2.66 ± 0.12	5.6%
2 wt. % silane	4.11 ± 0.14	2.58± 0.17	8.5%

TABLE 3.2 Creep correction for elastic modulus of room temperature water degraded samples.

It can be noted from table 3.2 that there was decline in reduction of elastic modulus for increased wt. % of silane in modified epoxy when subjected to water degradation. Introduction of water to epoxy modified with silane leads to hydrolysis of silane and thereby formation of silanols. Under influence of water degradation, epoxide rings present in epoxy can open up and lead to $O-H$ bond which will be instrumental to form covalent bonds with coupling agent.

Sample Type	50 ℃ water degraded Elastic Modulus (in GPa)		Reduction in elastic modulus on addition of silane
	Oliver Pharr method	Feng's creep correction	
Neat epoxy	4.42 ± 0.12	2.77 ± 0.14	-
0.5 wt. % silane	4.20 ± 0.18	2.67± 0.25	3.6%
1 wt. % silane	4.13 ± 0.08	2.63 ± 0.09	5%
2 wt. % silane	4.08 ± 0.11	2.54± 0.16	8.3%

TABLE 3.3 Creep correction for elastic modulus of 50 ℃ water degraded samples.

There was decrease in reduction of elastic modulus for modified epoxy samples that were subjected to 50 ℃ water degradation as wt. % of silane was increased. Formation of silanols under hygrothermal conditions lead to increased cross-linking in epoxy and thereby amount of degradation of resin was reduced.

Feng *et al.* had indicated that values of elastic modulus obtained through Oliver Pharr method will be 32 % more than its true value. In this study also we found that values of elastic modulus obtained from Nano indenter software that used Oliver – Pharr method was approximately 33% more than actual value of elastic modulus of the material. Theodore *et al.* reported elastic modulus of neat resin (EPON 862) as 3.4 GPa using flexural testing technique [42]. Elastic modulus of

EPON 862 evaluated using nanoindentation was 3.36 GPa and it was within 1 % of value obtained by flexural testing. Hence it is good to state that elastic modulus values obtained after applying correction for creep on nanoindentation data are very close to the true value.

It was interesting to note in fig. 3.4 that decrease in elastic modulus for 2 wt. % silane sample when subjected to hygrothermal conditions was only 6 % from ‘as is’ condition. But in the case of neat resin when subjected to water degradation, there was decrease of 17 % in elastic modulus. This signified the impact of presence of silane in modified epoxy when exposed to hygrothermal conditions.

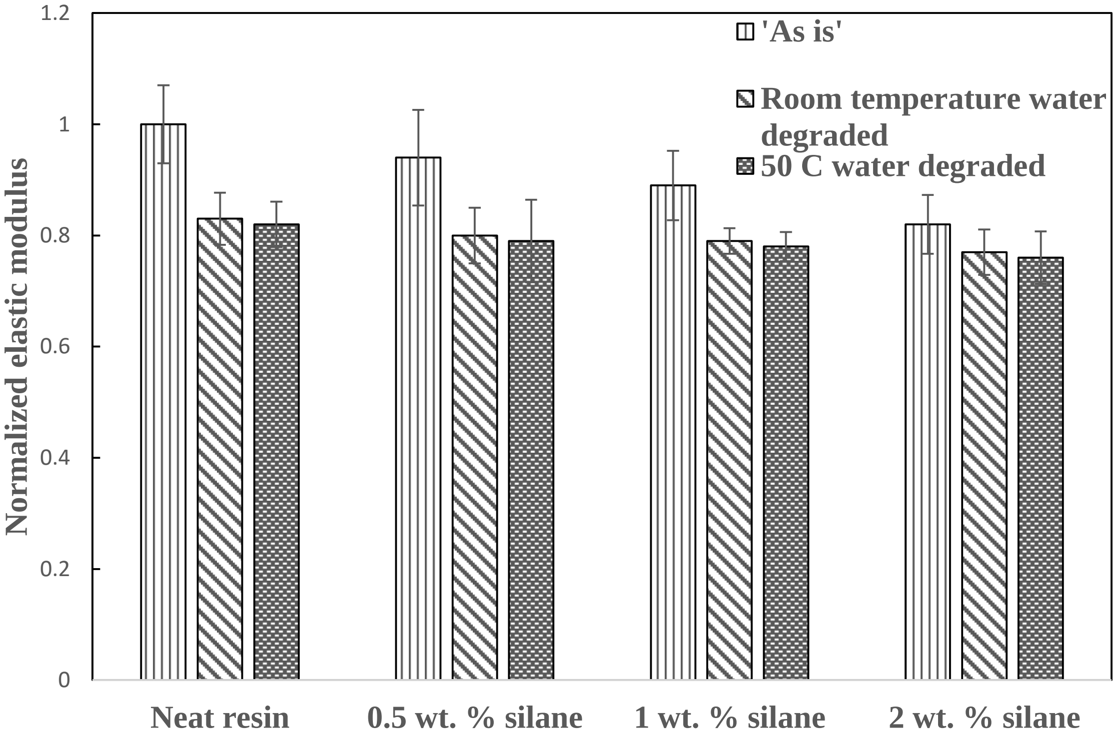

FIGURE 3.4 Change in elastic modulus for different environmental parameters

Decrease in modulus of epoxy on absorption of moisture content was reported previously by Ferguson *et al.* [17]. Shi *et al.* found that when the amount of moisture content and exposure temperature are increased, there was decrease in values of elastic modulus and hardness [43].

In this study also we can observe from figure 3.2 that decrease in elastic modulus was high for increase in moisture content at different temperature. This decrease in elastic modulus can be attributed to plasticization by water.

Hardness of all samples decreased over same period of time for different conditions applied as seen from the table given below.

Sample Type	Hardness of ‘as it is’ samples (GPa)	Hardness of room temperature water degraded samples (GPa)	Hardness of 50 ℃ water degraded samples (GPa)
Neat epoxy	0.240 ± 0.03	0.176 ± 0.01	0.158 ± 0.01
0.5 wt. % silane	0.209 ± 0.02	0.171± 0.008	0.140 ± 0.03
1 wt. % silane	0.189 ± 0.01	0.145 ± 0.01	0.129 ± 0.02
2 wt. % silane	0.166 ± 0.01	0.141 ± 0.01	0.126 ± 0.02

TABLE 3.4 Change in hardness of samples for three conditions used in study.

3.2 Creep compliance

Creep is a very important factor in evaluation of properties of time-dependent materials. Creep compliance can be used to quantify the ability of a material to flow on application of constant stress.

In this study it was assumed that epoxy exhibits linear viscoelastic behavior. Displacement data obtained during nanoindentation from the hold region of 50 seconds where constant load was applied on the sample was used to study the creep behavior. It was similar to the method by employed by Catherine Tweedie *et al.* to generate creep compliance curves for different polymers including epoxy [44]. Figure 3.5 to 3.7 shows the variation in creep compliance for different wt. percentages of silane added to neat resin under three environmental conditions that was used in this work. The values obtained in this study are in good agreement with creep compliance found for EPON 862 after curing under conditions close to room temperature in literature [45].

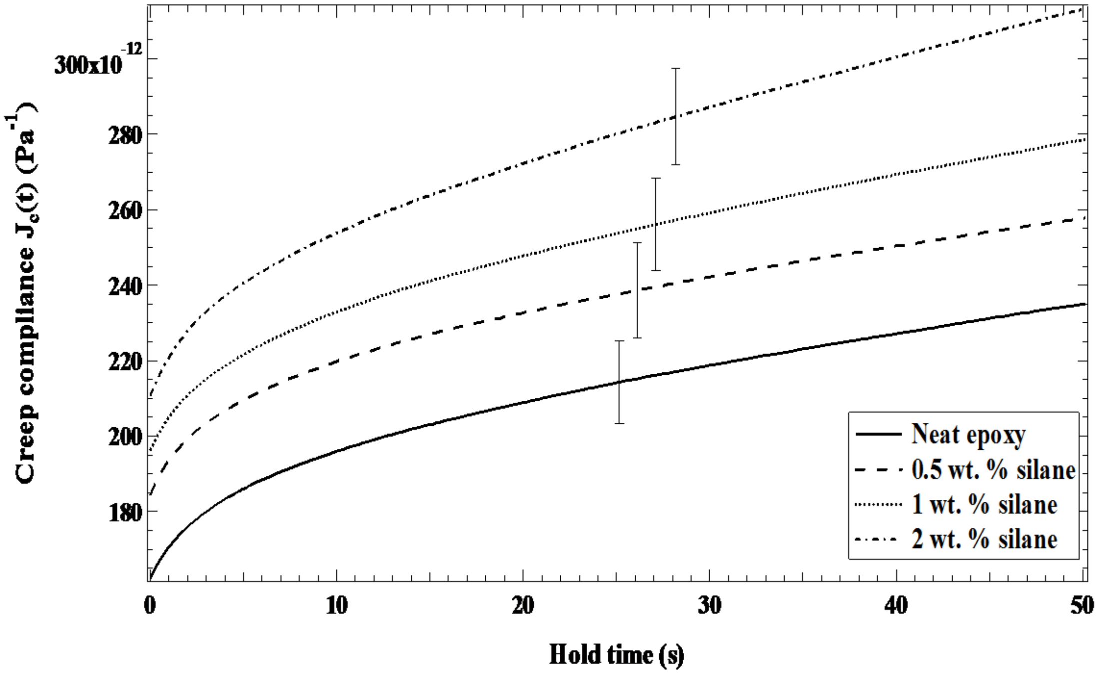

FIGURE 3.5 Variation in creep compliance for 'as is' samples

In 'as is' conditon, addition of silane to epoxy had made it more creep compliant. For 2 wt. % addition of silane there was approximately 38% increase in creep compliance from that of neat resin at the end of hold time. Similar phenomena was noted when samples were subjected to water degradation at room temperature as indicated in fig 3.6. It was observed that neat resin became more creep compliant i.e. by about 23% when exposed to water. However there was only marginal increase of 2 % in creep compliance of epoxy modified with 2 wt. % silane from 'as is' condition when exposed to water for the same period of time.

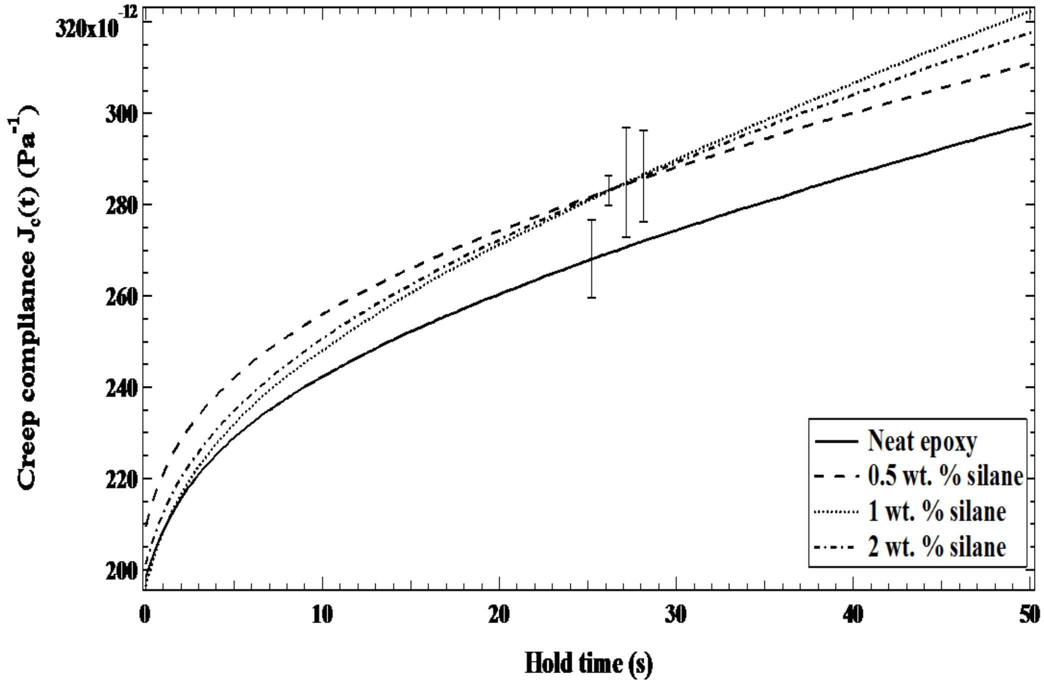

FIGURE 3.6 Variation in creep compliance for room temperature water degraded samples

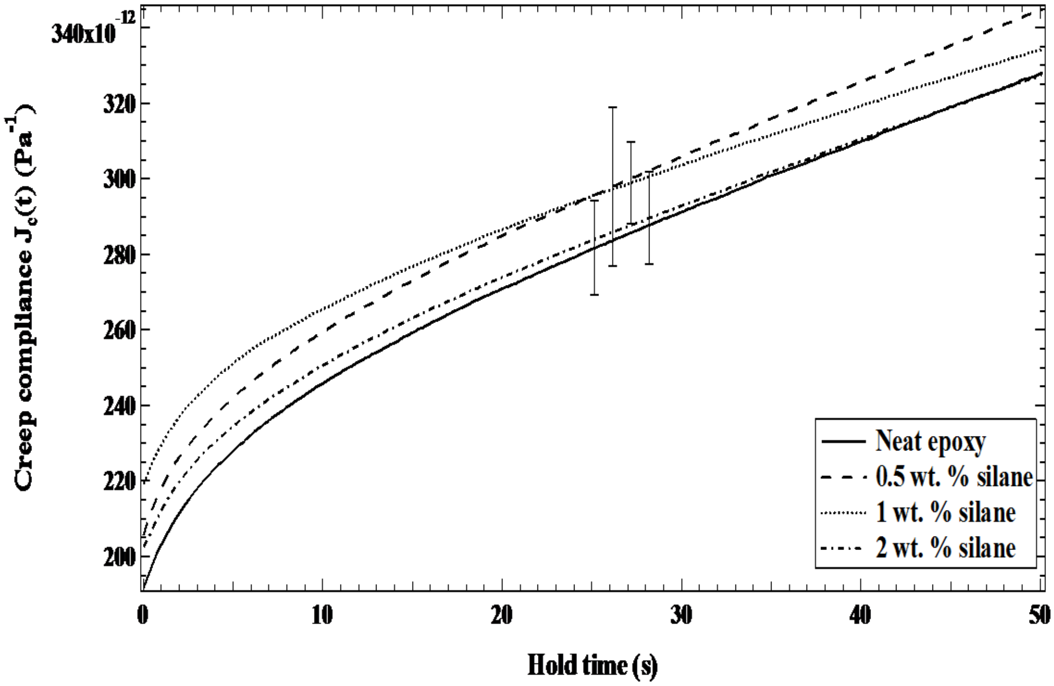

FIGURE 3.7 Variation in creep compliance for 50 ℃ water degraded sample

It can be noted from fig. 3.7 that increase in temperature had major influence on creep behavior of neat resin and modified epoxy. The increase in slopes of the curves from figs. 3.5 to 3.7 are an indicator of how rate of creep bahavior over the duration of hold period has been influenced by presence of water and rise in temperature. Neat epoxy became more creep compliant as temperature was increased to 50 ℃ during water degradation. It can be observed that there was nearly 40 % increase in creep behavior of unmodified epoxy. However, the most important aspect of fig. 3.7 was about how addition of silane influenced creep behavior of the material. It can be seen that as wt. percentage of silane was increased in the modified epoxy, it became more creep resistant under hygrothermal conditions. This behavior can be due to increased formation of silanols by hydrolysis of silane when exposed to water and high temperature. Presence of silanols increases the possibility of forming covalent bonds with epoxy and thereby increasing cross linking of epoxy in modified resin.

Zhou *et al*. has shown that silane was able to increase creep resistance of polypropylene over time. Increase in temperature of water degradation has also influenced the cross-linking of epoxy indicated by the fig. 3.7. It can be atrributed to increase in breaking of bonds and re-forming of bonds involving hydrolysis of silane and thereby increasing cross-linking in epoxy system.

3.4 Glass transition temperature

Glass transition temperature (T_g) range for a thermosetting polymer indicates the transition from 'glassy' or rigid state to more flexible or 'rubbery' state. Degree of curing impacts the glass transition temperature of neat epoxy resin. [46]. It was noted from [46] that upon moisture absorption glass transition temperature of epoxies will be reduced. Higher T_g values in epoxy indicates higher degree of cross-linking and better tensile properties at high temperatures. Differential scanning calorimetry was used to easily determine glass transition temperature (T_g) of the samples. Q2000 differential scanning calorimeter used in this study has precision of ± 0.01 ℃

in the measurement of temperature. Mean value of glass transition temperature range was obtained by using two tangents on flat slopes of the third cycle for which thermal history was known.

It was observed that glass transition temperature of modified epoxy decreased with increase in wt. percentage of silane added for ‘as is’ and room temperature water degraded samples. This closely matched with how elastic modulus changed on increasing the wt. percentage of silane in the samples. Addition of silane has lead to degradation of properties of neat resin.

Sample Type	Glass transition temperature (T_g) of ‘as it is’ samples (in ℃)	Glass transition temperature (T_g) of room temperature water degraded samples (in ℃)	Glass transition temperature (T_g) of 50 ℃ water degraded samples (in ℃)
Neat epoxy	56	55.50	55.43
2% silane	52.45	52.17	57.6

TABLE 3.5 Glass transistion temperature of samples

It can be noted from table 3.5 that glass transition temperature of neat resin decreased when it was subjected to water degradation. Effect of increasing temperature to 50 ℃ during water degradation resulted only in a marginal decrease of T_g value. There was 6 % decrease in glass transition temperature on addition of 2 wt. % silane to neat resin for ‘as is’ condition. A similar amount of decrease was observed for room temperature water degraded samples.

T_g of 2 wt.% silane sample increased by 4 % after being exposed to water at 50 ℃. The rise in temperature will help in opening of epoxide rings present in epoxy. This gives rise to presence of $O-H$ bond in substrate which will be used by silanols to form covalent bonds and thereby increase in cross-linking of epoxy. Increase in cross-linking of epoxy during water degradation at sub-boiling temperature can be understood by rise in T_g value. The increase in wt. percentage of silane into neat epoxy under sub-boiling tmeperature water degradation made modified epoxy more creep resistant, which is consistent with increase noted in T_g for 2 wt. % silane exposed to water at 50 ℃.

3.5 Fourier transform infrared spectroscopy (FTIR)

It was important to check if any chemical changes were occuring in bonds for all the samples after being subjected to different environmental conditions. Spectrographic methods provide wide range of IR bands which can be closely associated with molecular structure of different functional groups. There are characteristic vibration frequencies that are connected with particular group of atoms in compounds that will be utilised to understand change in spectra for the different samples [47]. FTIR spectra was expected to show formation of bonds that could possibly explain the variation in elastic modulus, creep compliance and glass transition temperature of the samples. It can be seen from figures 3.8 to 3.10 that there was no major change in spectra for the different samples that was used in the study.

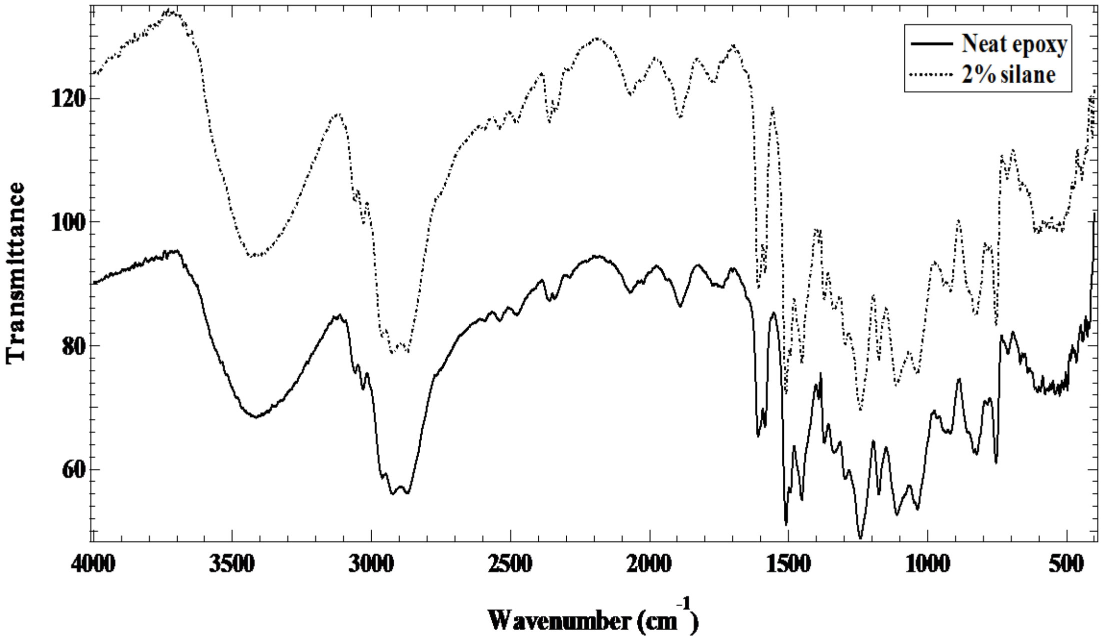

Figure 3.8 FTIR spectra of ‘as is’ samples

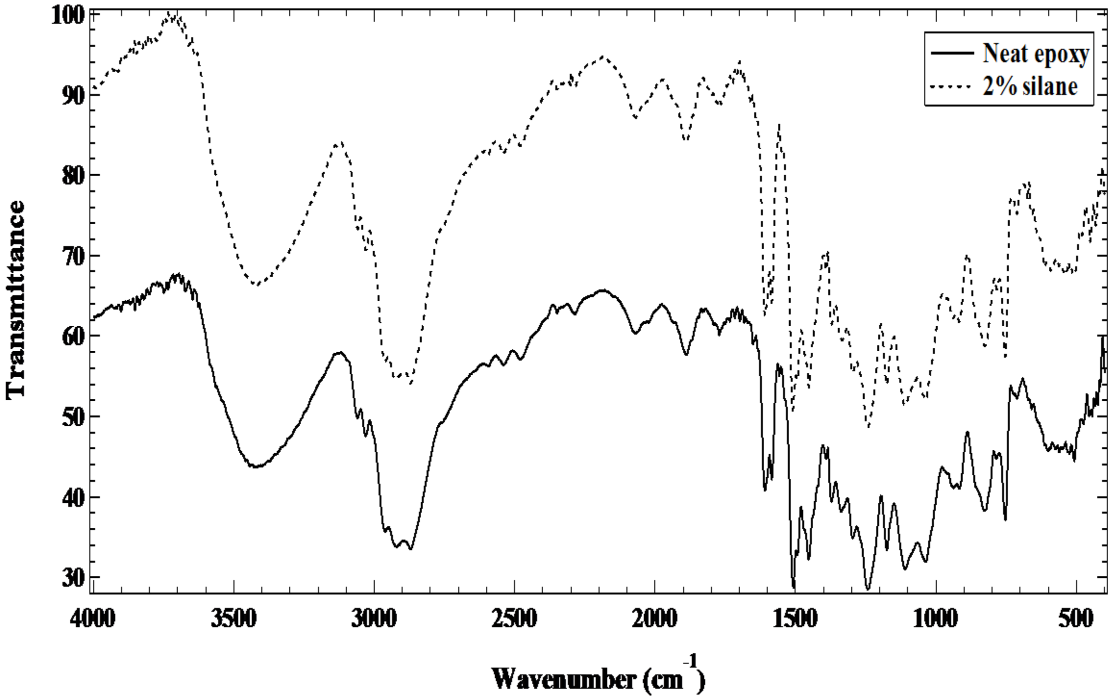

Figure 3.9 FTIR spectra of room temperature water degraded samples

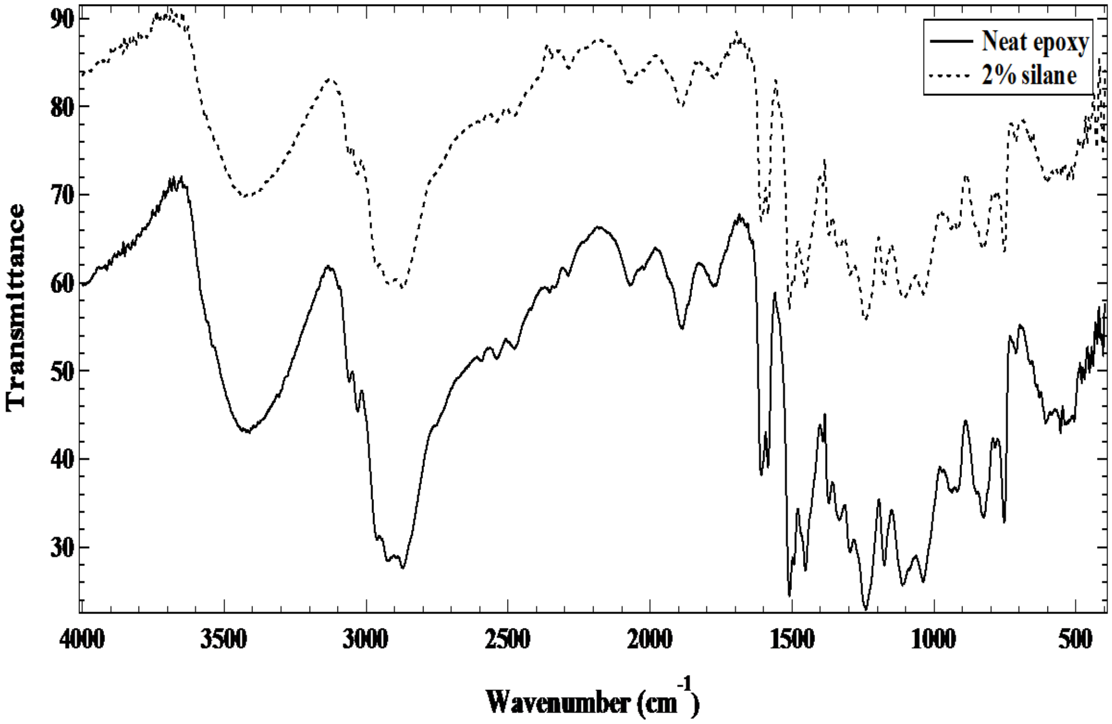

Figure 3.10 FTIR spectra of 50 ℃ water degraded samples

There were some minor alterations that was identified close to 1110 cm^{-1} and approximately 940 cm^{-1} wavenumbers. These correspond to $Si-O-Si$ and $Si-OH$ bonds [47]. But these cannot be ascertained as the reason for changes observed in previous sections.

The main region of interest was 1100 to 1150 cm^{-1} region in the spectra which corresponds to $Si-O-Si$ bonds that will be present after hydrolysis of silane. However we were not able to observe any major change in peaks in this region. This could be due to masking of the peaks associated with $Si-O-Si$ by other aliphatic epoxide groups which has IR spectra around the same region as there was significant amount of epoxide groups in the system. Formation of silanols also cannot be verified using the spectra obtained due to presence of other $O-H$ groups in the system.

Yang *et al.* had reported that there was no significant change in spectra when studying effect of amino based silane on epoxy resin even though there was significant change in properties exhibited by the material [33]. We had expected FTIR results to be more conclusive in this study due to increased compatability of silane coupling agent with epoxy due to presence of glycidyloxy groups.

It will be interesting to check if other spectrographic methods like solid state Nuclear Magnetic Resonance (NMR) can provide more understanding about the chemical changes behind the observations made in this study.

CHAPTER IV

CONCLUSION

One of the primary goal of this study was to explore the impact of adding silane on neat epoxy. It was important to understand the influence of (3 – Glycidyloxypropyl) trimethoxysilane, a common form of silane coupling agent on mechanical properties of neat resin. The glycidyloxy group present in coupling agent and epoxide ring in epoxy made it interesting to study the effect of silane on epoxy. Three conditions – 'as is', room temperature water degraded and 50℃ water degraded were used to analyze the variations in properties of samples made by modifying neat epoxy resin with silane added as 0.5, 1 and 2 wt. % respectively. Rate of water absorption under room temperature was increased by silane during 48 hours duration of water degradation. However, the influence of silane was not significant on percentage of relative water gain for sub-boiling temperature water degradation.

It was observed that addition of silane degraded the neat resin in 'as – is' condition. Results obtained from nanoindentation test showed that elastic modulus and hardness of the samples followed a decreasing trend as wt. % of silane in the sample was increased. However it was good to note that influence of silane added to neat resin was profound under hygrothermal conditions as the rate of decrease in value of elastic modulus was reduced significantly. The viscoelastic nature of epoxy was taken in to consideration by using the extension made to Oliver – Pharr method by Feng *et al.* for calculation of mechanical properties of the samples in this study. It provided more accurate values of elastic modulus of neat resin which was consistent with values reported so far.

The impact of silane under hygrothermal conditions on modified epoxy was also investigated in this study. Neat epoxy showed increase in creep behavior when subjected to water degradation at room temperature and 50 ℃. In 'as – is' condition it was noted that by increasing wt. % of silane the creep compliance of modified epoxy became higher. An interesting observation was that for sub boiling water degraded samples increasing wt. % of silane in modified epoxy made the material more creep resistant.

Differential scanning calorimetry (DSC) results indicated 7 % decrease in glass transition temperature (T_g) for 'as – is' condition when wt. % of silane was increased in modified epoxy. This proved that addition of silane degraded neat resin, which was consistent with interpretation of change in mechanical properties of modified epoxy. However it was noted that T_g increased for 2 wt. % silane after being subjected to 50 ℃ water degradation. It showed that addition of silane to neat resin had a positive impact under hygrothermal conditions.

FTIR results were expected to provide insight into chemical interactions that could be reason for the observations made in this study. We were mainly interested to see change in peaks around 1100 to 1150 cm^{-1} region which corresponds to $Si- O-Si$ bonds. However, we were not able to see any conclusive evidence from FTIR spectra of modified epoxy. The primary reason for this could be due to masking of change in chemical interaction at the same region of interest due to presence of large number of epoxide groups in the system. It will be interesting to note if other spectrographic methods like solid state NMR can reveal chemical changes which could be behind effect of silane on epoxy under hygrothermal conditions. Another interesting aspect will be to check if further increase in wt. % of silane has any effect on epoxy for same environmental parameters.

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