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Effect of excess silane on the viscoelastic behavior of epoxy under hygrothermal conditions

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Abstract

This study investigates the effects of excess organofunctional silane on the elastic and viscoelastic properties of an epoxy resin. Samples were prepared by adding 3–glycidoxypropyl trimethoxysilane (GPTMS) in varying amounts ranging from 0.5 to 8.0 wt. % to diglycidyl ether of bisphenol–F (DGEBF) epoxy cured using an amine-based hardener. Prepared samples were subjected to hygrothermal conditioning by immersion in water at 21°C and 50°C. Subsequently, instrumented nanoindentation was used to determine the elastic modulus and creep compliance. A Fickian model fitted to moisture absorption data indicates that after 48 hours specimens were fully saturated to a depth of approximately 150 μm, which is significantly higher than the maximum indentation depth of 1 μm. This implies that the indentation material response was determined from a fully saturated region. It was found that the addition of silane leads to a reduction in the elastic modulus. In the presence of hygrothermal degradation, this reduction still occurs but is less than the non-conditioned case, especially for exposure at 50°C. For example, the

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addition of 8.0 wt. % silane reduces the elastic modulus by an average of 70% as compared to the pristine sample, and conditioning at 21°C and 50°C results in reductions of elastic modulus by 73% and 52%, respectively. The overall reduction in the elastic modulus value is due to the inclusion of flexible silane into the epoxy resin. Under hygrothermal conditions, however, the hydrolysis of silane mitigates the reduction in elastic modulus, especially at higher temperature conditioning. The viscous response of the material is sensitive to the inclusion of silane and hygrothermal conditioning. However, at very low wt. % of silane (less than 2%), the material becomes creep resistant and at higher wt. %, the behavior is similar to the elastic modulus. Fourier transform infrared (FTIR) spectra indicates that *Si*–*Si* interaction becomes predominant at higher wt. fractions leading to softening of the material. Inclusion of silane also reduces the glass transition temperature, which supports the increase in flexibility of the polymer chain.

Keywords: A. Epoxides, Nanoindentation, Hygrothermal conditions, D. Elastic modulus, D. Viscoelasticity

1 Introduction

Coupling agents, such as organofunctional silanes, have been used extensively to enhance the adhesion and chemical affinity between organic matrices and inorganic fillers in polymer based composites [1–3]. In addition to the advantage of being readily available commercially, organofunctional silanes possess an organic group which can be selected in accordance with the organic matrix. The presence of three hydrolyzable groups that act as intermediates in the formation of silanol groups, are useful in forming bonds with inorganic substrates [4]. Therefore, silanes can be used as chemical bridges between the organic matrix and inorganic fibers or fillers. Silanes are used either by direct application to inorganic substrates, i.e. fiber surface treatments, or through matrix modifications [5].

Silane coupling agents have reportedly improved laminate properties in composites and have also found use as adhesion promoters. The influence of adding silane to an epoxy on the properties of carbon–epoxy composites was studied by Yang *et al.* [6] and they indicated improvement in flexural properties.

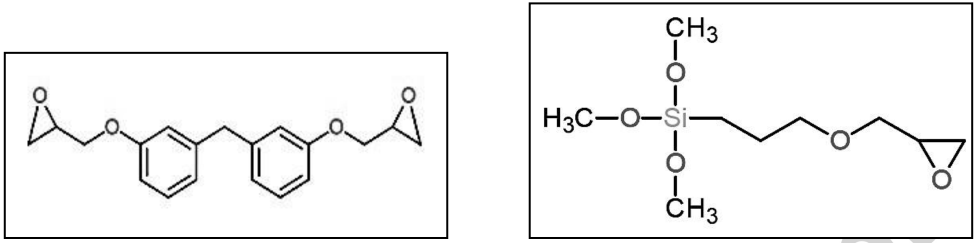
The effectiveness of silane coupling agents is dependent on the type of fiber used and the silane's compatibility with the matrix. For example, silanes are efficacious with glass and aluminum but inefficient with graphite and carbon black [7]. Suzuki *et al.* [8] reviewed the structure and various characterization techniques for the silane–matrix interphase. They suggested that a "different interphase" could exist due to the presence of an alternating copolymer or due to a terminal reaction between silane and matrix. Chiang *et al.* [9] discussed chemical bond formation between coupling agents and glass fibers. In addition, the interaction of organic resin with an organo-functional group present in the coupling agent was also explained. The formation of silanol groups through the hydrolysis of the three hydrolyzable components in the silane, is the most important intermediate step in the creation of reversible covalent bonds.

The presence of excess silane on glass fibers as condensed or free-form silanol groups has also been reported [10, 11]. These silane monomers and oligomers remain physisorbed on the inorganic fiber. Jensen *et al.* [12] examined the network formed by alkoxy silane–epoxy and observed that the modulus of an epoxy–silane network was lower than the modulus of the epoxy matrix. However, limited research exists that has focused on the effects of such excess silane on the resulting viscoelastic behavior of the epoxy–silane network, especially in the presence of hygrothermal conditions. This is the focus of the present investigation.

2 Materials and methodology

2.1 Sample preparation

In the present investigation, diglycidyl ether of bisphenol–F (DGEBF) based epoxy resin (EPON 862®) was cured using an aliphatic amine-based hardener (EPIKURE 3274®). Both epoxy and hardener were acquired from the Miller-Stephenson Chemical Company (Dunbury, Connecticut, USA). The organofunctional silane used in this study was 3–glycidoxypropyl trimethoxysilane (GPTMS) with the empirical formula as $C_9H_{20}O_5Si$ (Sigma-Aldrich Corporation, St. Louis, Missouri, USA). There are two reasons for selecting GPTMS. First, it is a methoxysilane, which is effective even under anhydrous conditions. Second, it exhibits good compatibility with epoxy [7]. The chemical structures of DGEBF and GPTMS are illustrated in Figs. 1a and 1b, respectively.



(a) DGEBF

(b) GPTMS

Figure 1: Chemical structures

Samples were prepared by adding the silane in varying weight amounts ranging from 0.5 to 8.0 wt. % to the epoxy resin. This was then hand-mixed and followed by mixing in a stoichiometric amount of the curing agent. The mixture was degassed under vacuum to remove entrapped air bubbles and poured into 25 mm diameter circular molds. Curing was first done at room temperature (21°C) for 24 hours followed by post curing at 121°C for 6 hours. Throughout the specimen preparation process the silane was handled in a glove box under an argon environment (UNILAB 2000, MBRAUN, Stratham, New Hampshire, USA) to prevent exposure to moisture present in ambient air. Finally, 2 mm thick disk-shaped specimens were cut from the cured 25 mm diameter cylinders using a low speed diamond saw (ISOMET 1000, Buehler, Lake Bluff, Illinois, USA). This was also done under dry conditions to avoid exposure to water. The specimens were then dry polished using an automated metallographic polisher (Labopol 5, Struers, Cleveland, Ohio, USA).

2.2 Hygrothermal conditioning

One batch of samples for each of the materials (0.5 to 8.0 wt. % silane) was immersed in water at room temperature (21°C). A second batch of samples from the same set of materials was immersed in water at 50°C temperature. Distilled water was used for both tests to avoid the influence of any minerals present in water on the hydrolysis of silane and its reaction with epoxy. The samples were conditioned for 48 hours at both immersion temperatures.

Samples were suspended in water using a loosely looped string in a conical flask. This was done to allow exposure of water on both surfaces. The surface area of the two flat regions, based on the average dimensions of 25.4 mm diameter and 2 mm thickness, was approximately 4000 mm^2 and the curved surface area was about 300 mm^2. As the surface area of the flat region was much greater than the curved region, it was assumed that the moisture absorption was one dimensional. For the experiments at 50°C, the conical flask was placed in a silicon oil bath to ensure uniform heating and to minimize temperature gradients in water. A condenser was used to trap, reclaim and reuse the water that evaporated from the conical flask. This ensured that the water level remained constant. At specified time intervals, including at the beginning and the end of the degradation test, samples were removed, wiped dry, and weighed using a precision analytical balance (Sartorius BP 301S, Sigma-Aldrich Corporation, St. Louis, Missouri, USA) to monitor weight gain due to moisture absorption.

2.3 Mechanical characterization

An MTS nanoindenter (Agilent Technologies, Santa Clara, California, USA) equipped with a Berkovich tip (half angle, θ = 70.3°) was used to perform load-controlled nanoindentation tests. The indentation experiments were carried out by applying a loading ramp at 0.1 mN/s to the peak load of 1 mN, a constant load hold for 50 s, followed by unloading again at 0.1 mN/s. Each sample was indented at 16 points, which were arranged in a 4×4 array with a distance of 10 μm between two indentation points. The load–displacement data from the experiments was used to determine the elastic modulus of the materials correcting for creep effects, as per the procedure attributed to Feng and Ngan [13]. As an extension to the Oliver–Pharr [14] method, Feng and Ngan proposed that the true stiffness, S is related to the apparent stiffness, S_u as,

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

where, $\dot{h}_h$ refers to indenter displacement rate at the end of the load hold and $\dot{P}$ is the unloading rate at the beginning of unload. The true stiffness was used to determine the elastic modulus of the sample as the modulus of the indenter was known.

Additionally, the same data was used to evaluate the creep compliance of those materials. Displacement data obtained from the constant load (hold) region of 50 s, was used to study the creep behavior. The process used was similar to the method employed by Tweedie *et al.* [15] to generate creep compliance ($J_c(t)$) curves for different polymers including epoxy. The creep compliance curves were modeled as,

$$J_c(t) = \frac{8tan(\alpha)h^2(t)}{\pi P_o} \tag{2}$$

where, $h(t)$ is the experimentally measured displacement during the hold time, α is the semi-apex angle for the Berkovich indenter with a value of 19.7°, and P_o is the constant load applied at hold.

2.4 Thermal and chemical characterization

A Q2000 calorimeter (TA Instruments, New Castle, Delaware, USA) was used to evaluate the glass transition temperature. Samples of 10 mg nominal weight were equilibrated to −15°C and subjected to isothermal conditioning for one minute. Then the temperature was ramped up to 200°C at a rate of 10°C/min and the sample was allowed to undergo an isothermal equilibration process for one minute. This cycle was used to erase any previous thermal history of the sample. Subsequently, the sample was then again cooled to −15°C at a rate of 10°C/min followed by isothermal conditioning for one minute. Finally, the new thermal history of the sample was specified and was used to obtain the glass transition temperature (T_g) from the heat flow–temperature plot. Here, the temperature of the sample was increased to 200°C at a rate of 10°C/min and then subjected to the isothermal process for a one minute time span.

An FTIR spectrometer (Varian 680-IR, Agilent Technologies, Santa Clara, California, USA) was used to perform absorbance mode FTIR spectroscopy. Potassium bromide (KBr) was used for providing background to the spectra. Sample mixtures were prepared by dispersing approximately 5 mg of powdered material in circa 95 mg of KBr using a pestle and mortar. The spectra consisted of peaks varying from wavenumbers 4000 cm^{-1} to 400 cm^{-1}. A characteristic IR chart was used to interpret the spectra of each sample.

3 Results and discussion

3.1 Water transport

Table 1 lists the weight gains of samples subjected to moisture absorption at 21°C and 50°C. Both the addition of GPTMS to epoxy and an increase in conditioning temperature led to increased moisture absorption. This weight gain data was fitted using a Fickian diffusion model given in Eq. (3), to determine M_∞, the maximum moisture content absorbed at saturation, and D, the diffusion coefficient. The average values of M_∞ and D for samples water conditioned at 21°C were obtained as 0.02 g and 4.56×10^{-4} mm²/h, respectively.

Table 1: Weight gain of samples subjected to moisture absorption at 21°C and 50°C

Sample	Weight gain (%)	
	21°C conditioning	50°C conditioning
Neat resin	0.19 ± 0.03	1.38 ± 0.08
0.5 wt.% silane	0.35 ± 0.08	1.48 ± 0.06
1 wt.% silane	0.36 ± 0.04	1.56 ± 0.09
2 wt.% silane	0.32 ± 0.12	1.54 ± 0.11
4 wt.% silane	0.38 ± 0.05	1.57 ± 0.10
8 wt.% silane	0.44 ± 0.06	1.60 ± 0.12

Analysis of weight gain of samples conditioned at 50°C lead to average value of M_∞ and D as 0.07 g and 1.07×10^{-3} mm²/h, respectively.

$$\frac{M_t}{M_\infty} = \frac{4}{h}\sqrt{\frac{Dt}{\pi}} \tag{3}$$

Using the values of M_∞ and D, we can predict the saturation depth for each of the samples at 48 hours for water conditioning at 21°C and 50°C. The saturation depth range for 21°C water conditioned samples ranged from 147 μm to 166 μm. Similarly, it was found that at 48 hours, the saturation depth range for 50°C conditioning was from 252 μm to 260 μm. As the saturation depth range for all the water conditioned samples at 48 hours is significantly higher than the maximum indentation depth of 1 μm, the material properties determined using indentation correspond to a fully saturated region.

3.2 Mechanical properties

3.2.1 Elastic modulus

Load–displacement curves obtained from nanoindentation were used to determine mechanical properties of silane modified epoxy. Prior research has shown that the use of the Oliver–Pharr approach overestimates the values of elastic modulus by up to 33% for materials that exhibit a viscoelastic response [16]. Therefore, the correction proposed by Feng and Ngan [13] was employed in this study. This approach resulted in elastic modulus values that are within 10% of those determined by flexural testing [17].

Table 2: Normalized elastic modulus of samples subjected to different environmental conditions

Sample	Normalized elastic modulus		
	as prepared	21°C conditioning	50°C conditioning
Neat resin	1.00 ± 0.06	0.89 ± 0.02	0.76 ± 0.04
0.5 wt.% silane	0.90 ± 0.05	0.84 ± 0.06	0.75 ± 0.03
1 wt.% silane	0.92 ± 0.05	0.83 ± 0.05	0.71 ± 0.02
2 wt.% silane	0.66 ± 0.06	0.83 ± 0.06	0.72 ± 0.03
4 wt.% silane	0.80 ± 0.05	0.77 ± 0.07	0.84 ± 0.06

8 wt.% silane	0.30 ± 0.04	0.27 ± 0.03	0.48 ± 0.04

Table 2 lists the variation in elastic modulus values of different specimens. The elastic modulus values were normalized with respect to the elastic modulus of as-prepared and neat epoxy to provide ease of comparison. The decrease in elastic modulus of neat epoxy due to water absorption is consistent with literature and it is generally attributed to plasticization [18, 19]. It was also observed that with increasing silane loading, the modulus values of epoxy resin decreased monotonically. At 8.0 wt. % of silane reinforced epoxy, the modulus decreased by 70%, which is quite significant. This reduction was due to an increase in chain flexibility upon the addition of silane.

Under hygrothermal conditioning, however, the hydrolysis of silane can lead to an increase in covalent bonding, which can mitigate the loss of elastic modulus due to plasticization of epoxy. Accordingly, it is observed in Table 2 that the decrease in modulus is less when the samples are subjected to hygrothermal conditioning, especially at elevated temperatures. The elastic modulus of 8.0 wt. % silane loaded samples that are exposed to water at 50°C conditioning reduced only by 52% as compared to the 70% reduction which happened in the absence of hygrothermal conditions. The elevated temperature leads to the opening of epoxide rings in the silane and promotes enhanced interaction with epoxy resin. This curing of silane loaded epoxy results in the formation of new covalent bonds, which may be the reason for relatively higher modulus values under hygrothermal conditions.

3.2.2 Creep compliance

Figures 2, 3 and 4 show the variations of creep compliance as functions of silane loading for the as-prepared, 21°C water conditioning, and 50°C water conditioning cases, respectively. The values of creep compliance at the end of the hold period are listed in Table 3. For the case of as-prepared samples, the creep compliance values obtained for epoxy resin were in good agreement with published literature [20]. This provides confidence in the experimental procedure and the model used to quantify the creep compliance curves.

As shown in Fig. 2, the addition of silane led to a monotonic increase in the values of creep compliance. However, the changes for 0.5 wt. % and 1.0

wt. % were comparatively small. Addition of 0.5 wt. % and 1.0 wt. % silane caused an increase by an average amount of 6% and 9% in the creep compliance at the end of the hold time. In contrast, for 2.0 wt. %, 4.0 wt. %, and 8.0 wt. %, the values increased by an average of 42%, 71%, and 417%, respectively. Enhanced silane–silane interaction due to the abundance of epoxide groups led to this increase in creep compliance.

Table 3: Average creep compliance values at the end of hold time

Sample	Creep compliance ($\times 10^{-10}$ Pa^{-1})		
	as prepared	21°C conditioning	50°C conditioning
Neat resin	2.24 ± 0.31	2.56 ± 0.16	2.50 ± 0.49
0.5 wt.% silane	2.37 ± 0.18	1.99 ± 0.28	2.23 ± 0.55
1 wt.% silane	2.45 ± 0.24	1.89 ± 0.32	2.38 ± 0.45
2 wt.% silane	3.24 ± 0.93	2.03 ± 0.22	2.16 ± 0.29
4 wt.% silane	3.89 ± 0.44	2.95 ± 0.31	2.93 ± 0.52
8 wt.% silane	11.60 ± 1.17	15.80 ± 1.28	7.05 ± 0.95

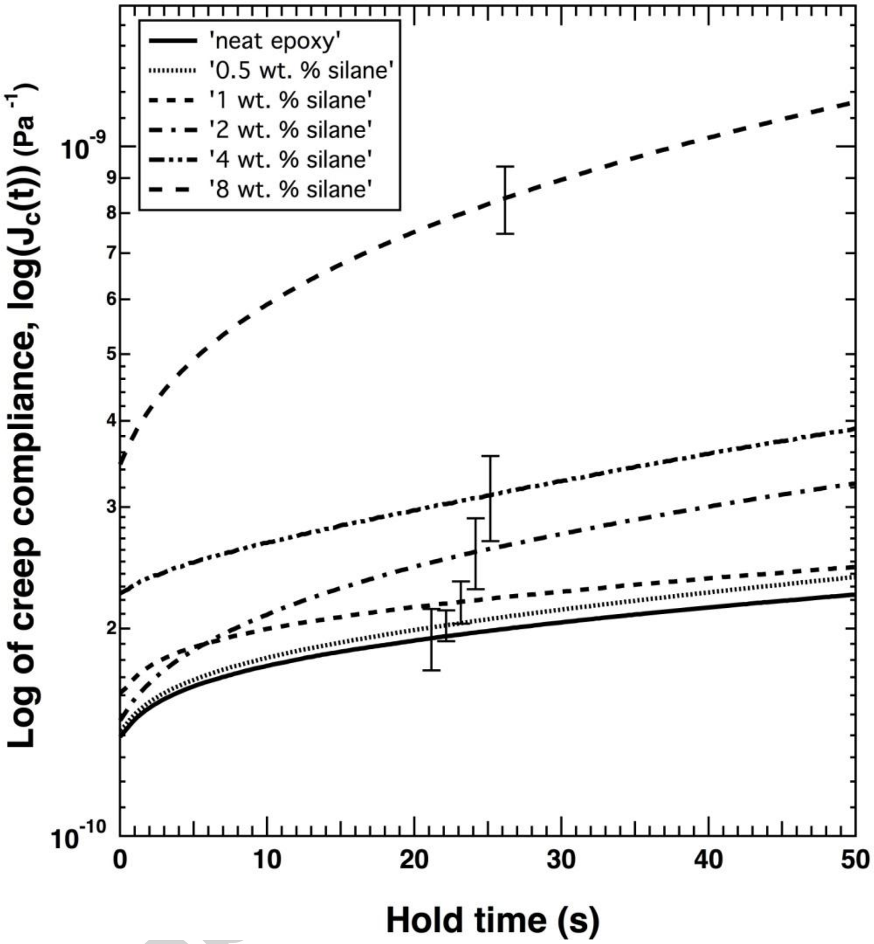


Figure 2: Creep compliance curves of as prepared samples measured as function of silane wt. %. Addition of silane makes the system progressively creep compliant.

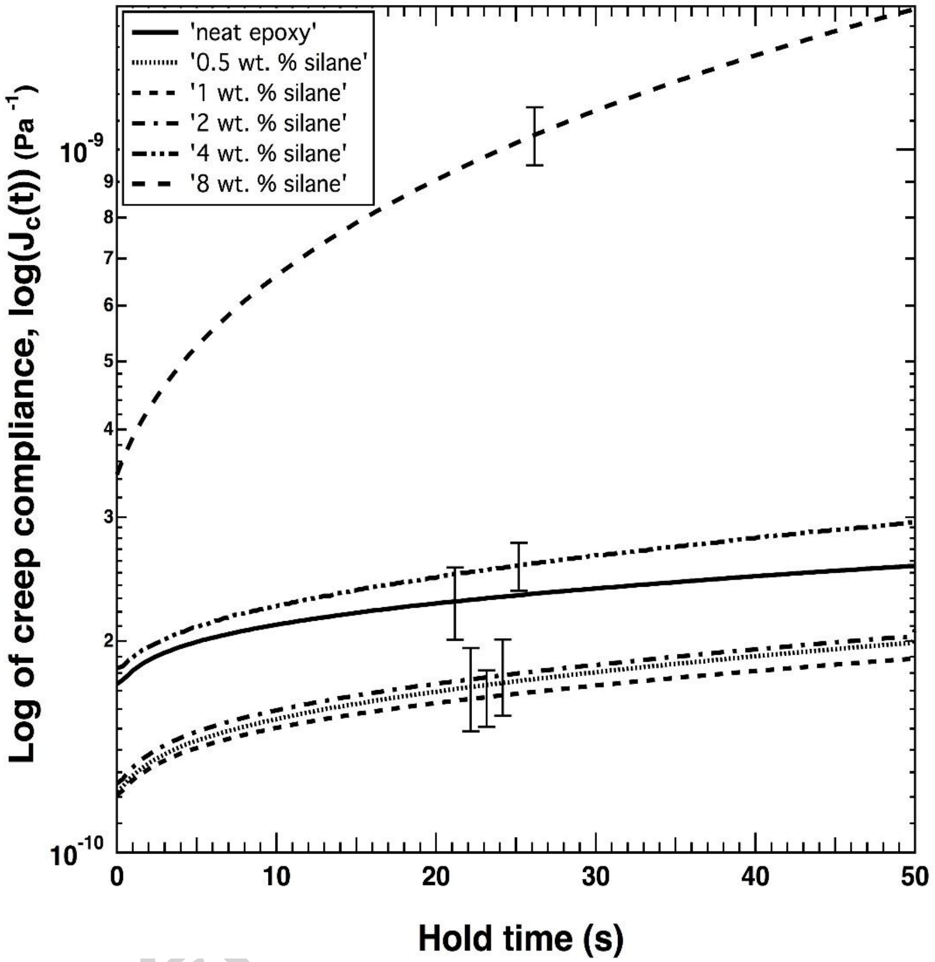


Figure 3: Creep compliance curves of 21°C water conditioned samples. Influence of hydrolysis of silane is overshadowed by abundance of silane.

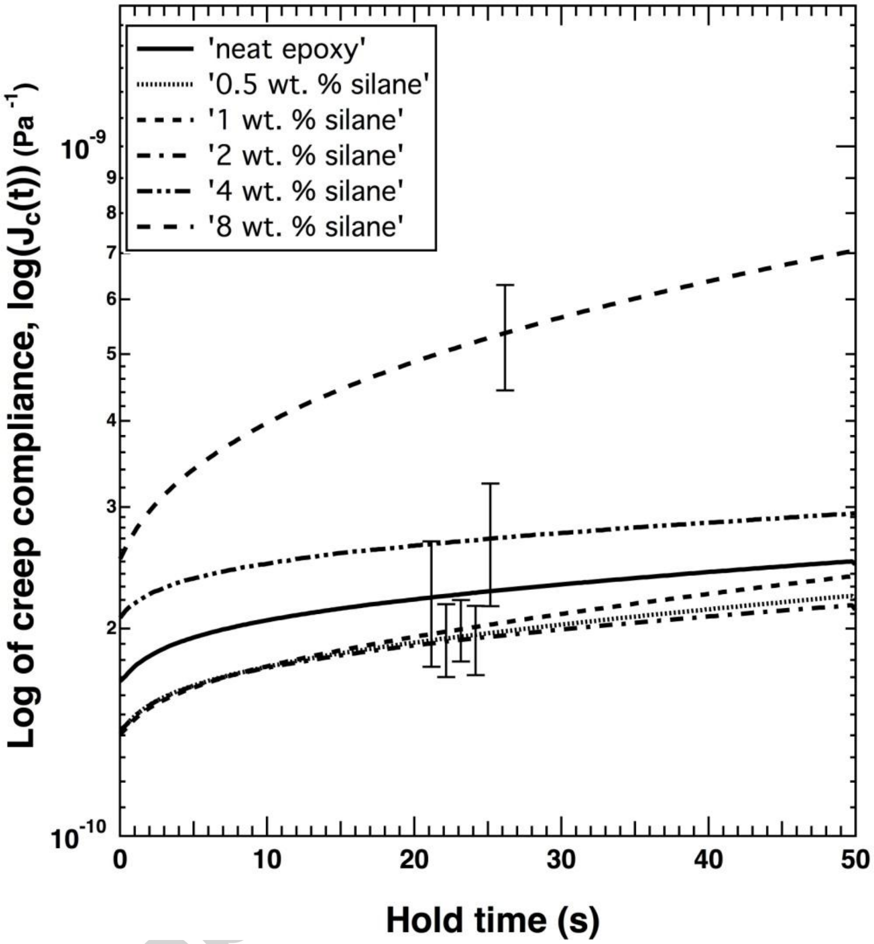


Figure 4: Creep compliance curves of 50°C water conditioned samples. Impact of moisture and temperature on interaction of silane with epoxy is captured.

Figure 3 shows the variation in creep behavior of materials that were hygrothermally conditioned at 21°C. It was observed that unaltered epoxy became more creep compliant, when exposed to moisture. At lower weight percentages of silane, such as 0.5 wt. %, 1.0 wt. %, and 2.0 wt. %, the creep compliance values at the end of 50 s decreased by 22%, 26%, and 20%, respectively. However, upon the addition of 8.0 wt. % silane, the creep compliance increased by 500%!

At lower weight percentages of silane addition, the hydrolysis of silane leads to silane–epoxy interaction which results in the formation of covalent bonds. The hydrolysis of silane involves four steps that take place in quick progression and result in the formation of covalent bonds with the epoxy resin, as discussed in detail by Arkles [7]. Silanol (Si−O−H) containing entities are formed by the hydrolysis of alkoxy groups. These condense to oligomers which include siloxane linkages (Si−O−Si). Hydroxyl groups present in the resin help in hydrogen bonding with these oligomers. Subsequently, these oligomers cure to result in reversible covalent bonds with the resin. These hydrolysis of silane is operative at all added percentages. But in the case of high weight percentages of silane loading, the abundance of epoxide groups in the system leads to predominant silane–silane interaction, which overshadows or hinders the silane–epoxy interactions due to hydrolysis.

Figure 4 shows the impact of temperature on the creep behavior of materials, coupled with moisture absorption. Inclusion of silane in epoxy at low wt. % (less than 2%) made the material creep resistant as compared to the neat epoxy, after 50°C conditioning. The rise in temperature leads to increased rates of hydrolysis of silanol groups and higher rates of curing, leading to higher levels of silane–epoxy interaction. For higher weight percentages of silane addition such as 4.0 wt. % and 8.0 wt. %, the creep compliance values increased by 17% and 182%, respectively. Similar to the 21°C conditioning, the silane–silane interaction was more dominant of the two competing interactions in the case of silane loading at higher wt. percentages.

3.3 FTIR spectra

Figures 5 and 6 show the FTIR spectra under as-prepared, 21°C water conditioning, and 50°C water conditioning cases, for epoxy containing 2.0 and 8.0 wt.% silane loading, respectively. Each peak and wavenumber denotes a certain form of bond or element present in the sample. Data for neat epoxy, for each of the three cases, is included in both Figs. 5 and 6 to aid in comparison.

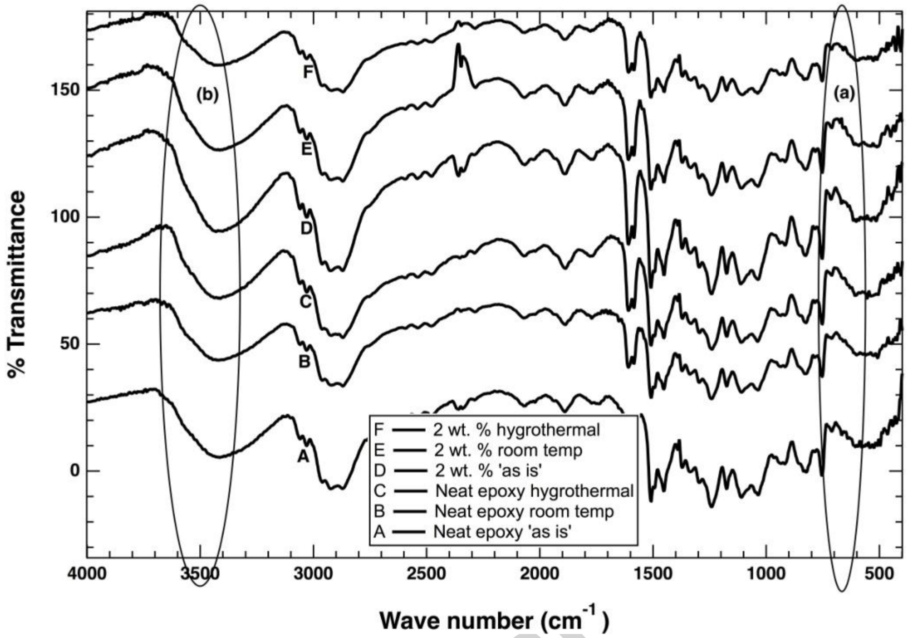


Figure 5: FTIR spectra of neat epoxy and 2.0 wt. % silane loading under as-prepared, 21°C water conditioning, and 50°C water conditioning.

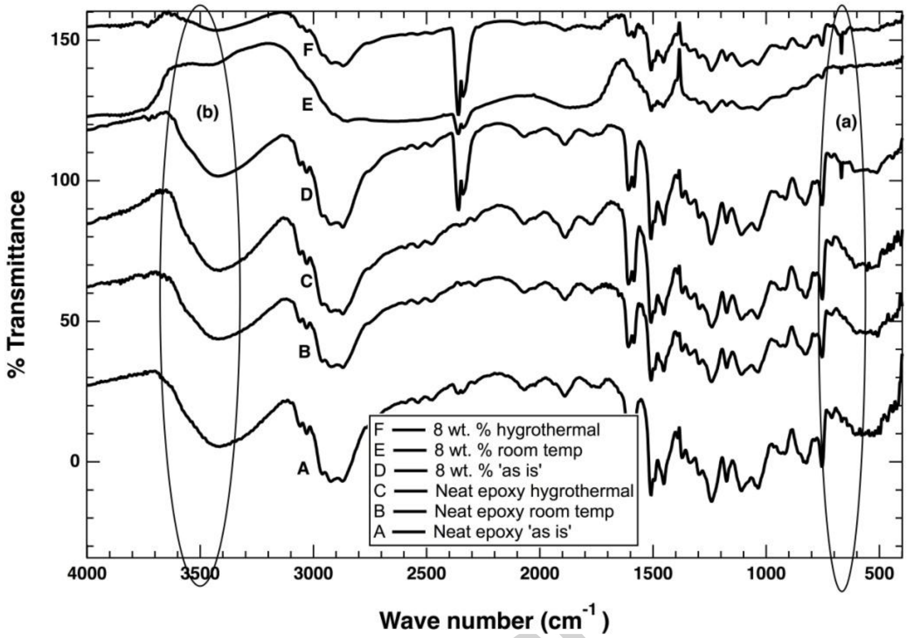


Figure 6: FTIR spectra of neat epoxy and 8.0 wt. % silane loading under as-prepared, 21^{o}C water conditioning, and 50^{o}C water conditioning.

The peak around 600 cm^{-1}, as indicated by region (a) in both figures, represents the Si−Si bond. This peak is not observed for the case of neat epoxy or for 2.0 wt. % silane added epoxy, as shown in Fig. 5, which indicates the lack of silane–silane interaction. However, this peak is observed for 8.0 wt. % silane added epoxy under all the three conditions, as shown in Fig. 6. Silane–silane interaction was responsible for influencing the elastic modulus and creep compliance of 8.0 wt. % silane added epoxy. The silane–silane interaction leads to formation of more compliant chemical structures leading to decreased elastic modulus and increased creep compliance.

The peak around 3500 cm^{-1}, as indicated by region (b) in both figures, represents the −OH bond. The intensity of this peak was reduced for the case of 2 wt. % and 8 wt. % silane added epoxy under water conditioning, as shown in Fig. 5 and 6, respectively, which indicates Si−OH interaction. The hydrolysis of silane was responsible for the improved creep behavior of low wt. % silane loaded epoxy under water conditioning. The peaks around

1110 cm^{-1} and 940 cm^{-1} represent Si−O−Si and Si−OH bonds, respectively. However, these peaks are not distinguishable for silane added epoxy due to the masking of the peaks by other aliphatic epoxide groups, which are present in abundance in the system. Higher loading of silane leads to a greater masking effect by epoxide groups.

3.4 Glass transition temperature

The glass transition temperature (T_g) range for a thermosetting polymer indicates the transition from a glassy to a rubbery state. Table 4 illustrates the influence of silane loading and hygrothermal conditioning on the glass transition temperature of epoxy. The T_g value of the as prepared epoxy resin was found to be 78.62°C. Under the influence of moisture, it can be noted that the T_g value of pristine epoxy dropped by an average of 26% and 21% for 21°C and 50°C conditioning, respectively. This change is signified by the decline in properties of epoxy due to break down of cross-linking structures formed during curing, which is consistent with the results reported by Danieley et al. [21].

Addition of silane to epoxy under as-prepared condition decreased its T_g and it was approximately halved with addition of 8.0 wt. % silane. This reduction in the glass transition temperature is due to the increased chain flexibility caused by significant silane–silane interaction. A similar trend was observed in the elastic modulus values mentioned in previous section. However under the influence of water conditioning, it can be noted that T_g of 2.0 wt. % silane added epoxy has changed very less. This is due to silane–epoxy interaction caused by hydrolysis of silane, which is consistent with its creep behavior. But due to the increased silane–silane interaction in the 8.0 wt. % silane added epoxy, even after water conditioning it's T_g decreased by 40%.

Table 4: Change in normalized T_g of samples subjected to different environmental conditions

Sample	Glass transition temperature, T_g (°C)		
	as prepared	21°C conditioning	50°C conditioning

Neat resin	1.00 ± 0.02	0.74 ± 0.04	0.79 ± 0.02
2wt. % silane	0.84 ± 0.03	0.80 ± 0.02	0.78 ± 0.04
8wt. % silane	0.53 ± 0.02	0.51 ± 0.03	0.60 ± 0.04

4 Conclusions

The effect of excess 3–glycidoxypropyl trimethoxysilane, a common silane coupling agent, was studied on the elastic and viscoelastic properties of an epoxy resin under exposure to hygrothermal conditioning. The silane was added in different wt. percentages between 0.5 and 8.0 to the epoxy under an inert atmosphere. The elastic and viscoelastic properties were investigated under three different environmental conditions: as-prepared, 21°C water conditioning, and 50°C water conditioning. Instrumented nanoindentation was used to determine the elastic modulus and creep compliance of the samples. As the saturation depth range for all the water conditioned samples at 48 hours was significantly higher than the maximum indentation depth, the material properties determined using indentation corresponded to a fully saturated region.

The elastic modulus of the epoxy–silane system was significantly lower than that of the pristine epoxy due to the increased flexibility of the polymer chain with the addition of more epoxide groups. However, it was found that the elastic modulus of epoxy–silane materials decreased at a much lower rate under hygrothermal conditions due to silane–epoxy interaction. The hydrolysis of silane leads to the formation of irreversible covalent bonds that will decrease the degradation of epoxy due to excess silane, under hygrothermal conditions.

The influence of silane and hygrothermal conditions on the viscoelastic response of epoxy was studied by generating creep compliance curves using displacement data obtained from constant-load nanoindentation. The results showed that the material became more creep compliant with increased silane loading for the as-prepared condition due to Si−Si interaction. However, under hygrothermal conditions, the creep compliance value at the end of hold time, for lower weight percentages of silane loading (less than 2%) decreased with respect to the corresponding epoxy resin. The hydrolysis of silane leading to predominant silane–epoxy interaction was responsible for the trend reversal. For higher weight percentages of silane addition, however, there was an increase in creep compliance behavior due to increased Si−Si interaction. In the FTIR spectra, the peak corresponding to Si−Si interaction around 600 cm^{-1} was observed only for the 8.0 wt. % silane loaded sample. Si−Si interaction was responsible for the lowering of elastic modulus and increased creep compliance of the 8 wt. % silane added epoxy. The intensity of the −OH bond near 3500 cm^{-1} decreased for 2 wt. % and 8 wt. % silane added epoxy under hygrothermal conditions, which indicates the influence of Si−OH interaction. However, Si−O−Si and Si−OH bonds were not captured due to the masking of its peaks by the abundance of aliphatic epoxide groups in the system. T_g of the samples decreased due to the impact of silane loading and water conditioning. It was consistent with the variation in stiffness observed for all the samples under the three conditions.

The focus of this study was to characterize the influence of silane loading and hygrothermal conditions on the elastic and viscoelastic behavior of a silane-epoxy interphase that can exist due to fiber surface treatments or sizing. It was found that lower weight percentages of silane loading (less than 2%) can mitigate the effects of hygrothermal degradation whereas higher silane loading further exacerbates the deterioration of properties. At lower wt. % loadings the hydrolysis of silane leads to increased silane–epoxy interactions resulting in enhanced cross-linking. At higher wt. % loadings the hydrolysis of silane still occurs but is overshadowed by the presence of Si−Si interactions that lead to chain flexibility and a reduction in elastic modulus and increase in creep compliance.

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