

Lifetime Prediction of Nano-Silica based Glass Fibre/Epoxy composite by Time Temperature Superposition Principle

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Abstract: The incorporation of nano fillers in Fibre reinforced polymer (FRP) composites has been a source of experimentation for researchers. Addition of nano fillers has been found to improve mechanical, thermal as well as electrical properties of Glass fibre reinforced polymer (GFRP) composites. The in-plane mechanical properties of GFRP composite are mainly controlled by fibers and therefore exhibit good values. However, composite exhibits poor through-thickness properties, in which the matrix and interface are the dominant factors. Therefore, it is conducive to modify the matrix through dispersion of nano fillers. Creep is defined as the plastic deformation experienced by a material for a temperature at constant stress over a prolonged period of time. Determination of Master Curve using time-temperature superposition principle is conducive for predicting the lifetime of materials involved in naval and structural applications. This is because such materials remain in service for a prolonged time period before failure which is difficult to be kept marked. However, the failure analysis can be extrapolated from its behaviour in a shorter time at an elevated temperature as is done in master creep analysis. The present research work dealt with time-temperature analysis of 0.1% SiO₂-based GFRP composites fabricated through hand-layup method. Composition of 0.1% for SiO₂ nano fillers with respect to the weight of the fibers was observed to provide optimized flexural properties. Time and temperature dependence of flexural properties of GFRP composites with and without nano SiO₂ was determined by conducting 3-point bend flexural creep tests over a range of temperature. Stepwise isothermal creep tests from room temperature (30°C) to the glass transition temperature T_g (120°C) were performed with an alternative creep/relaxation period of 1 hour at each temperature. A constant stress of 40MPa was applied during the creep tests. The time-temperature superposition principle was followed while determining the Master Curve and cumulative damage law. The purpose of a Master Curve was to determine the variation of compliance with respect to increase in time and temperature of the specimen. The shift factors at any reference temperature were determined by Arrhenius activation energy method at a far lower temperature than T_g (Glass transition temperature) and by manual shift method at a temperature near T_g (Glass transition temperature).

1. Introduction

Studies to determine the short-term as well as the long-term durability of various types of fiber reinforced polymer (FRP) composites are being conducted widely. This is due to the fact that the composite structure may be prone to failure at longer durations of time under a constant stress. The viscoelastic behavior of the polymer matrix further leads to a gradual deterioration of the composite material under adverse environmental conditions and for longer durations if not for sudden failure. The glass transition temperature (T_g) exhibited by the polymer matrix is defined as the temperature above which the transition in the amorphous regions between the glassy and rubbery state occurs[1]. It is observed that due to drastic structural changes above the T_g , structural properties of the composites deteriorate significantly. Therefore, inference can be made that the suppletion temperature of a composite be maintained below the glass transition temperature for satisfactory mechanical performance and creep resistance.

2. Materials and methods

2.1 Materials

The resin (Diglycidyl ether of Bisphenol A based epoxy) and curing agent (Triethylene tetra amine) used in this study were supplied by Atul Industries, India under the trade names Lapox L12 and K6 respectively. The glass fiber (3 K plain weave E-glass) having a filament diameter of about 15 μm , was purchased from Owens Corning, India. Areal weight of this fabric was 360 g/m²,



composed of 16 and 14 yarns/inch in warp and weft directions respectively. Silica having spherical structure with diameter in the range of 15–30 nm was received in the powder form from Sigma Aldrich Pvt. Limited.

2.2 Creep: Creep can be defined as the tendency of a material to deform permanently under the influence of mechanical stresses owing to long term exposure to high levels of stress[2]. For a perfectly elastic material (both linear and non-linear), strain(ϵ) is a time-independent property and is directly related with the applied stress (σ)

Polymers such as epoxy exhibit viscoelastic properties. They store elastic energy within themselves when deformed and utilize this energy to revert back to their original form after the deforming stress is removed. Above a certain temperature, they behave as liquids and exhibit viscosity. Here, their deformation becomes time-dependent.

Here, $S(t)$ is termed as the creep compliance, which can be defined as the inverse of stiffness, but here it is a time-dependent function:

$$S(t) = \frac{\epsilon(t)}{\sigma} \quad (1)$$

It takes a general polymeric material around tens of thousands of years to deform and is therefore impractical to be determined through long-term creep testing till the completion of the designated lifetime of the specimen. Thus, an accelerated creep testing on materials at an elevated temperature over a shorter period of time is conducted, and the results are extrapolated to ascertain the behaviour of materials at room temperature for an elongated period of time.

2.3 Time-Temperature Superposition model (TTSP) :

Based on TTSP, it is possible to generate short-term creep model at various temperatures and a master curve is generated accordingly. Master creep generation involves a shift parameter (a_T) that matches the creep behavior at a reference temperature [3]. According to the TTSP principle, the frequency function of a dynamic property (say compliance S) at one temperature T_{ref} is similar in shape to the same function in neighboring temperatures. Therefore, $S(t)$ versus logarithmic frequency (or logarithmic response time) at one temperature can be horizontally shifted along the reduced time axis and made to overlap at the neighboring temperatures. This shift distance along the reduced time axis is called the shift factor (a_T) and is given as

$$a_T = \frac{t}{t_r} \quad (2)$$

Where t is the generated time steps for a temperature, t_r is the reduced time corresponding to the reference temperature T_{ref} [1].

In the TTS diagram, the curve at every temperature can be shifted at a horizontal distance to overlap the curve at the reference temperature (T_{ref}) at the neighboring temperature. In this way, for every reference temperature chosen there is a fully overlap curve, termed as the master curve.

3. Experimental Procedure

3.1 Specimen Preparation:

3.1.1 Preparation of SiO₂ nano filler modified epoxy resin:

169 g was taken and preheated at 120°C at 400rpm for half an hour. 0.1%weight of SiO₂ with respect to weight of 5-layers of glass fiber laminate was measured and was added to the epoxy resin, and stirred for 3 hours, followed by 1 hour of sonication after which the modified epoxy resin was placed in a vacuum chamber for 18 hours, in order to remove air bubbles.

3.1.2 Fabrication of the FRP composite with and without hybridized epoxy resin:

Fabrication of 5 layer laminate of bidirectional GFRP composite was conducted placing the epoxy resin (without/with nano-Silica) uniformly between each layer of glass fibers, one after the other. The composite was then cured in a hot press for 20 minutes to solidify the specimen. The finished sample was then kept at room temperature for 24 hours. Following this, specimens were cut and polished following ASTM B7264 standard. Polishing was followed by post curing in a hot air oven at 140°C for 6 hours, in order to facilitate cross-linking of the resin.

3.2 Testing conditions:

Determination of creep/relaxation isotherms were performed in a 3-point bending jig. Stepwise isothermal creep tests from room temperature (30°C) to glass transition temperature T_g (120°C) with an increment of 5°C at each step were performed with an alternative creep/relaxation period of 1 hour each at each temperature. A constant stress of 40MPa was applied during the creep tests and data points were taken after every 15 seconds. The T_g of the specimen was determined by conduction of DMA analysis through $\tan \delta$ peak method determined at various frequencies.

3.3 Calculations:

Creep compliance is determined from the equation:

$$D_c(t) = \frac{4bh^3\delta(t)}{PL^3} \quad (3)$$

where $D_c(t)$ is creep compliance (1/MPa) at a given time t ; P is the constant load (N) [4].

4. Result and Discussion

Determination of Flexural Creep at elevated temperatures:

It is highly impractical to determine the design lifetime of a material by conducting creep tests for the entire period. Therefore, prediction of durability is conducted using time-to-failure methods for a given load at elevated temperatures.

Figure 1 shows the creep compliance curve versus the actual time for the neat as well as Nano Silica modified GFRP specimens. The breaks between successive curves are an indication of the alternate recovery periods whereby data points have not been recorded.

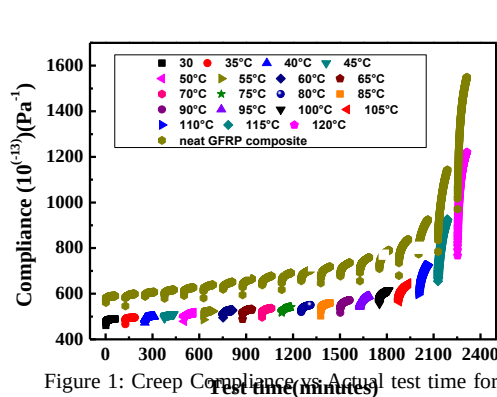


Figure 1: Creep Compliance vs Actual test time for nano modified GFRP and neat GFRP composite.

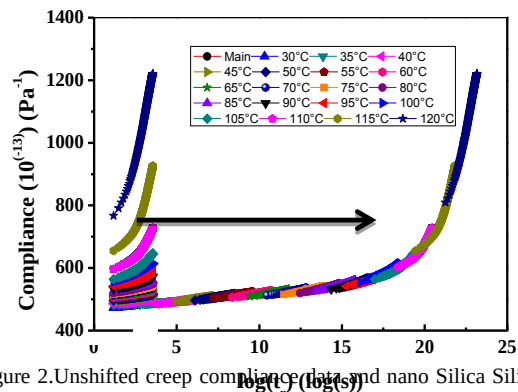


Figure 2: Unshifted creep compliance data and nano Silica modified GFRP composite master curve for $T_{ref} = 30^\circ\text{C}$

where t is the actual test time while t_r is the reduced time.

The reduced time is nothing but an expansion of the time scale at an isothermal reference temperature while generation of the master curve, and is given as

$$\log(t_r) = \log(t) - \log(a_T) \quad (4)$$

The creep compliance is not shifted for the reference temperature T_{ref} , since $\log a_T$ is zero. For all the other temperatures, the creep compliance curve is shifted horizontally on the reduced time (t_r) scale as is determined by the shift factor. For temperatures greater than T_{ref} , the curve is shifted to the right, since a_T is negative. Similarly, for temperatures less than T_{ref} , the curve is shifted to the left, since in this case a_T is positive. In case of manual shift factor method, the shift factors are chosen by hand so that the isothermal curves overlap in the subsequent temperatures.

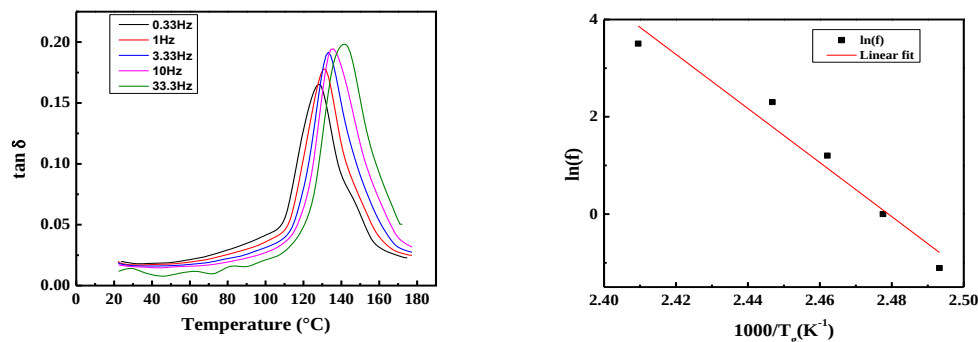


Figure 3(a). $\tan \delta$ curve peak T_g (b) variation of T_g as obtained by $\tan \delta$ peak for nano Silica modified GFRP composite

In case of activation energy method, it is possible to determine shift factors by the activation energy measured from the glass transition relaxation. The activation energy for glass transition can be measured from the slope of $\ln(f)$ vs $1/T_g$ graph as shown in Figure 3. Here, T_g is measured as each of the peak values of $\tan \delta$ vs temperature graph for various assigned frequencies (0.33Hz, 1Hz, 3.33Hz, 10Hz and 33.3Hz). Graph shown in Figure 3(a) is obtained by conduction of dynamic mechanical analysis[5].

The equation for calculation of activity is given by

$$\Delta H = -R \frac{d(\ln(f))}{d(1/T_g)} = - (8.314 \times 10^{-3}) (-55.60084 \times 10^3) = 462.06 \text{ KJ/mol} \quad (5)$$

The determination of activation energy in this manner makes the task of obtaining shift factors much easier as there is no requirement of generating the master curve in this case.

The shift factor is determined using time-temperature superposition model[1]. Using the constant activation energy technique, shift factor can be calculated by the following formula.

$$\text{Log}(a_T) = \frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \log e \quad (6)$$

This is derived from the Arrhenius relationship.

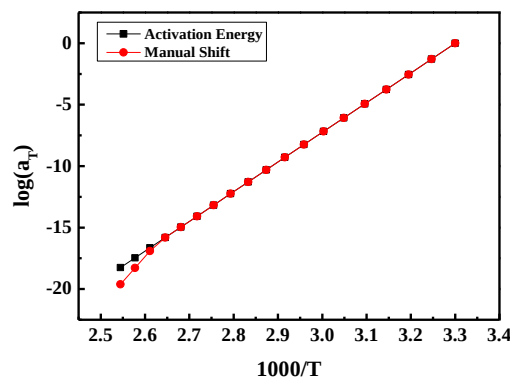


Figure 4. Shift factors versus $1/T$ for manual shift and constant activation energy estimation of for nano Silica modified GFRP

It has been observed that this equation is valid only up to a certain temperature below T_g , above which William-Landers-Ferry model (WLF) is applicable [6]. In case of nano Silica modified GFRP composite, the activation energy obtained is 462.06 KJ/mol.

As inferred from Figure 4 it had been observed that the manual shift factor and the constant activation energy shift factor coincide well upto $1000/T = 2.6$, which is $T = 111.6^\circ\text{C}$. Above this, the manually shifted data exhibits larger values of shift factor.

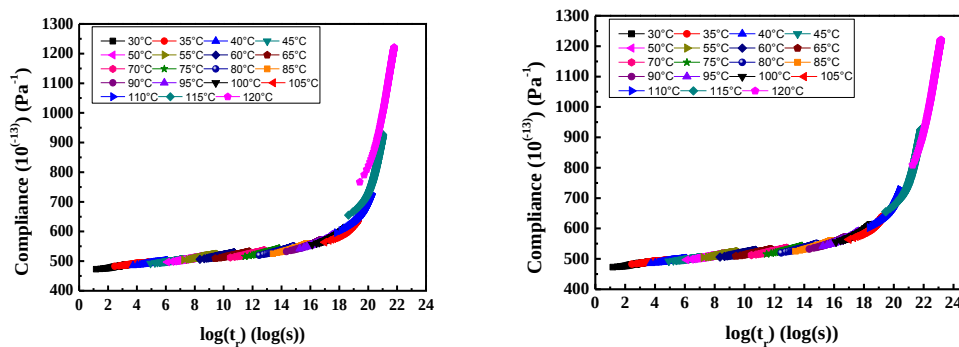


Figure 5. Master Curve for nano Silica modified GFRP at $T_{ref}=30^{\circ}\text{C}$: (a) constant activation energy (b) manual shift

It can be well deduced that constant activation energy curve falls invalid near temperature just below T_g , i.e. 115°C . Below this temperature range, the compliance data line quite well up, and starts to get distorted above it as shown in Figure 5(a).

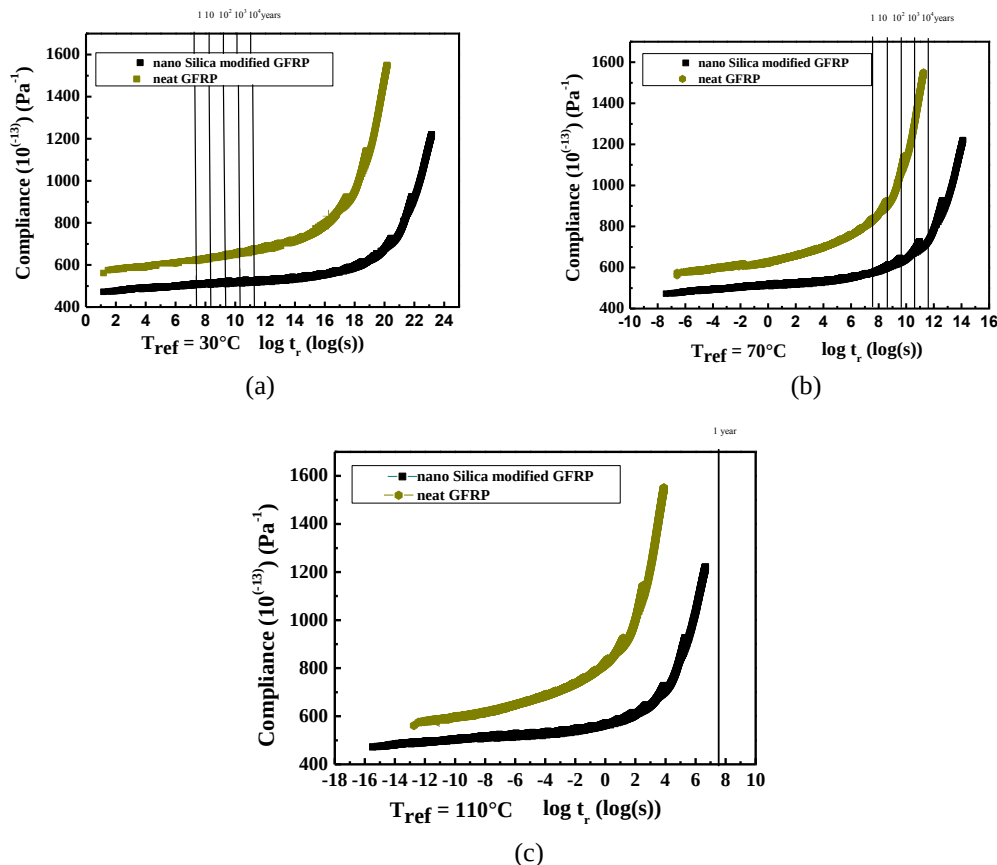


Figure 6. Master Creep Curve for nano Silica modified GFRP and neat GFRP at (a) $T_{ref} : 30^{\circ}\text{C}$ (b) $T_{ref} : 70^{\circ}\text{C}$ (c) $T_{ref} : 110^{\circ}\text{C}$

The lifetime prediction of the SiO_2 -modified GFRP composites have been done by using reference temperatures of 30°C , 70°C and 110°C along with a time sequence of 1, 10, 100, 1000 years and so on.

A comparative study of the master curves for the two specimens, first being the neat GFRP composite and the second being the nano-Silica modified GFRP composite indicates a similar yet distinguishable

difference in compliance with respect to time in case of three reference temperatures ($T_{\text{ref}} = 30^{\circ}\text{C}$, 70°C and 110°C) as shown in Figure 6.

5. Conclusions

The study of master creep analysis of a 0.1%SiO₂-modified Glass fiber/epoxy composite was conducted at various reference temperatures for a prolonged duration of time at a constant stress. The following conclusions were drawn:

- The constant activation energy method stands valid only up to a temperature far lower than T_g of the material after which the manual shift factor method provides more consistent master curve plot.
- A total of three master curves ($T_{\text{ref}} = 30^{\circ}\text{C}$, 70°C and 110°C) were generated using each method of shift factor estimation. The adequate model gives an important curvature of the master curve, due to the stress sensibility exponent of the model. It was inferred that the flexural creep strain is both time and temperature dependent, and becomes more viscoelastic near T_g .
- A comparative study between neat GFRP and nano-Silica modified GFRP composites showed that nano-Silica modified GFRP composite has a better stiffness (lower compliance) as compared to neat GFRP composite and therefore is more resistant to deformation than the latter.
- Lifetime prediction at various reference temperatures indicate that the modified GFRP can be sustained at room temperature for a high period of time (around 10,000 years) without exhibiting any significant change in the compliance. At a reference temperature of 70°C , durability up to 10 years is observed beyond which the compliance increases (i.e. stiffness decreases) drastically. At an elevated temperature of around 110°C , both the composites fail to sustain even for 1 year.

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