Effect of post-curing on thermal and mechanical behavior of GFRP composites

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Abstract. Curing cycle has a strong impact on the thermal and mechanical behavior of thermosetting polymers. The extent of cross-linking which is a strong function of curing temperature and time is directly linked to the glass transition temperature (T_g) of the thermosetting polymer. This transition temperature speaks about the transformation of the polymer from glassy state to rubbery state, hence decides the applicability of the material at certain temperature with certain degree of safety and reliability. Hence assessment of T_g and its possible improvement is quite essential from material point of view. The present study is emphasized on the impact of post curing parameters on thermal as well as mechanical behavior of glass fiber reinforced polymer (GFRP) composite. Post curing was carried out at 3 different temperatures (80°C, 110°C and 140°C) for different time periods (2h, 4h, 6h, 8h and 12h). Short beam Shear (SBS) test was performed on each of the post cured samples to determine the apparent Interlaminar Shear Strength (ILSS) and the corresponding T_g was also evaluated using differential scanning calorimetry (DSC) analysis. The results revealed that the ILSS and T_g are significantly affected with post curing parameters. No significant change in ILSS was obtained at 80°C over the entire curing time. In case of 110°C a smooth increment in ILSS was observed with time (even till 12 hrs). For samples post cured at 140°C a rapid improvement in ILSS takes place with time followed by saturation. With all the possible combinations of curing temperature and time, optimum values are noticed at 140°C for 6 hrs.

1. Introduction

Composite materials can be defined as a combination of two or more materials that results in better properties than those of the individual components used alone. These materials have high strength and stiffness combined with low density compared to the conventional metals. Polymers are structurally more complex than metals. Polymer – matrix composites are viscoelastic materials and their mechanical properties are significantly influenced by temperature. They are used mostly in areas from aerospace, automobiles and boats to cryogenic equipment such as cryogenic fuel tanks, cryogenic fuel delivery lines, cryogenic wind tunnels and parts of the cryogenic side of turbo-pumps because of their ease of handling, low fabrication cost and excellent mechanical properties [1].Curing is an irreversible reactionwhere chemical covalent cross-links are formed whichare thermally and mechanically stable. The curing process plays a major role in achieving the final mechanical properties and chemical resistance of the material. State of polymer resin is liquid (soft) before the fabrication of composite, which then changes to solid matrix (hard) after curing.For the fabrication of composite, two types of resins are used i) primary resin (matrix) ii) secondary resin (hardener). Most commonly used primary resins are epoxy, unsaturated polyester and polyurethane. Secondary resin i.e. hardener is added for curing purpose. Most commonly used secondary resin includesamines or peroxides. During cross-linking, the stateof matrix changes from liquid to gel and then transforms into solid. Curing can be done at room temperature as well as at elevated temperature [2].This depends on composition of resin and hardener. Optimum curing results in a perfectly cross-linked polymer network which leads to increased T_g and mechanical properties.The T_g depends on different factors, including composition of the resin molecule, curing agent, curing time, cross-linking density and temperature [3]. Generally, during post curingthe $T_g$increases with increasing post curing temperature but it will not exceed the cure temperature. There are several parameters that define the post-cure process. Two biggest variables are temperature and time, but also the time between initial curing and post curing and temperature profile gradient play a role. So, post curing process can play crucial role in obtaining optimum mechanical and thermal properties of polymer matrix composites [4]. Present investigation

includes the effect of two most primary post curing parameters, post curing temperature and time on the ILSS and T_g of GFRP composite and an attempt has been made to mathematically describe the variation of ILSS and T_g with post curing time at different temperatures.

2. Materials and experimental methods

2.1 Materials

Diglycidyl ether of Bisphenol A (DGEBA) based epoxy resin was used as matrix and triethylene tetra amine (TETA) was used as hardener. Resin and hardener were provided by Atul Industries Ltd, Gujarat under the trade name of Lapox L-12 and K-6 respectively.E-Glass fibres used were manufactured by Saint-Gobain. The reinforcement was used in the form of glass fibre sheets (3k, plain weave).

2.2 Fabrication of GFRP Composite

Woven fabric E- glass fibre were cut into the size of 25 cm X 25 cm to form 14 layer sheets and weighed by using electronic weighing machine. Epoxy resin was weighed to be 40% of the total weight of the fibre. Then hardeneris added which is equal to 10% of the weight of epoxy resin. Glass fibre/epoxy laminate have been prepared by hand lay-up method and cured in a hydraulic press by at 60°C temperature and 1MPa pressure for 20 minutes. Table 1 represents the properties of epoxy resin and glass fibre.

Figure 1. Glass/fibre composite before post curing and after post curing

Table 1. Properties of epoxy resin and glass fibre

Property	Epoxy	Glass Fibre
Tensile Strength (GPa)	0.11	3.4
Tensile Modulus (GPa)	4.1	72.3
Poisson's Ratio	0.3	0.2
Strain at Failure %	4.6	4.8
Density g/cm^3	1.162	2.58

2.3 Experimental methods

2.3.1.Post Curing schedule

The dried GFRP specimens were post cured in an oven at 80°C, 110°C and 140°C for 2h, 4h, 6h, 8h and 12h. The heating rate was 2°C/min. The specimens were cooled in oven atmosphere.

2.3.2. Short Beam Shear (SBS) test

The test was performed in 3 point bending fixture of Instron 5967 UTM using ASTM D2344-84 standard specimens to evaluate the apparent interlaminar shear strength.The tests were carried out at ambient temperature and at 1mm/min loading rate. The span to thickness ratio was kept 6.

2.3.3. Thermal analysis

DSC is a thermal analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature or time. DSC wascarried out in a nitrogen atmosphere. The weight of the samples was taken around 15 mg. Heating was performed from 30°C to 150°C with heating rate of 10°C/min. The glass transition event is observed as an endothermic step wise increase in the heat flow. Glass transition temperature represents the region in which the resin transforms from a hard glass solid to a viscous liquid.

3. Results and discussion

3.1 Effect of temperature and time on ILSS

Post cured samples showed change in colour in contrast to the non-post cured samples as shown in figure 1. A substantial increment in maximum stress value is observed in case of post curing the GFRP sample at 140 $^{\circ}$C for 2 hrs in comparison to the control sample, followed by a small increment with time which can be observed from figure 2 (a). After certain time period, the stress-strain curves overlap on each other indicating saturation in the strength value. Figure 2(b) represents stress-strain curves of samples cured at 80,110and 140°C for 6 hrs. No significant change in maximum stress values was observed at 80°C curing temperature. Gradual increment in maximum stress was further noticed on increasing curing temperature. Variation in ILSS forGFRP composite at different time periods is shown in figure 3. At 80°C temperature, no significant improvement in ILSS was noticed even after 12hrs of conditioning,because the ILSS mainly depends oncross-linking density at interface region.
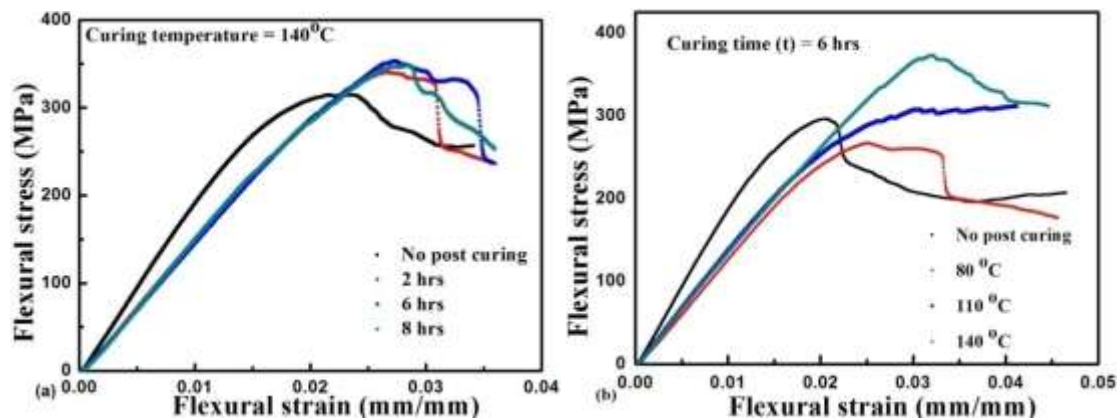

Figure 2. Effect of temperature and time on flexural stress.a) at 140°C for 2hrs, 6hrs and 8 hrs. b) at 80°C, 110°C and 140°C for 6hrs.

The energy available at these post curing parameters may not be sufficient to further enhance the wettability at the fibre/matrix interface, which in turn reflects no improvement in ILSS.At 110°C the ILSS increases with time steadily at a very slower rate. Here the variation in ILSS with time may be represented with a linear equation (i) as

$$ILSS\ (MPa)\ =\ 23.96\ +\ 1.24t\ (hrs)\text{-------- (i)}$$

At 110°C, the heat energy may be sufficient for the movement of polymeric chains at the interface for formation of certain cross-links and the density of the crosslinks at the interface gradually increases with time. Hence steady increment in ILSS is noticed with time.At 140°C, a very drastic increment was noticed inILSS at an earlier stage.
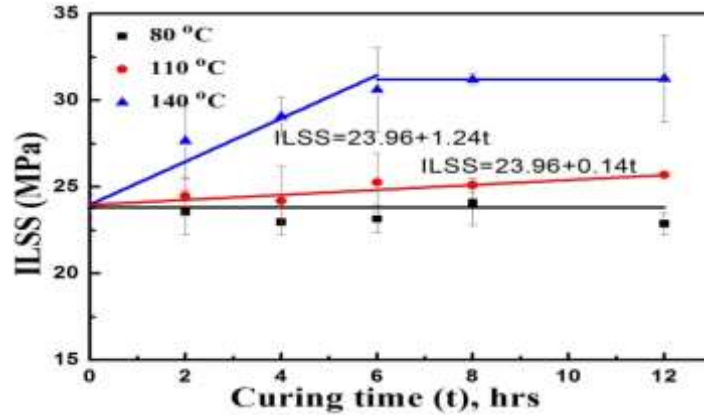
Figure 3. Effect of temperature and time on ILSS

A linear trend is noticed as shown in equation (ii) as

$$ILSS\ (MPa)\ =\ 23.96\ +\ 1.24t\ (hrs)\text{--------- (ii)}$$

The crosslink density at the interface increases rapidly with time and gets saturated after certain time period. Hence a drastic improvement in ILSS at the rate of 1.24 MPa/hr is noticed till 6 hrs of curing and then onwards saturation follows with an ILSS of approximately 31.45 MPa, which accounts for 25% higher than that of without post-cured GFRP.

3.2 Effect of temperature and time on T_g

The DSC curves for various curing temperature and time is plotted in figure 4. T_g is obtained from the onset of change in slope of the heat flow vs. temperature. Hence the variation in T_g with different curing time at different curing temperatures is reported in figure 4(a) and 4(b). Primarily the T_g of the composite is governed by the bulk polymer matrix. The variation of T_g when plotted against post curing time for various temperatures, it followed sigmoid curve as per the equation (iii).
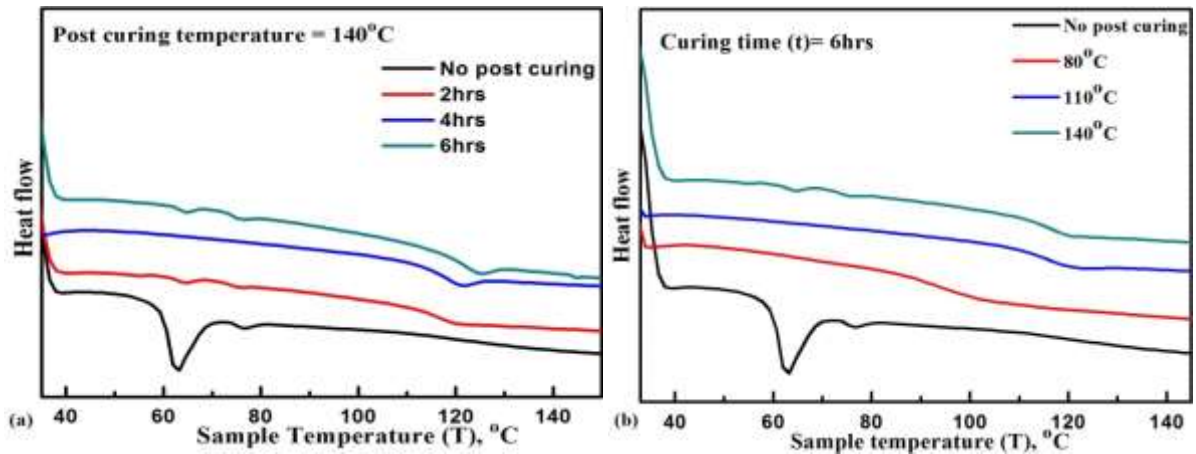

Figure 4. DSC curves for various post cured GFRP samples a) at 140°C for 2hrs, 4hrs and 6 hrs. b) at 80°C, 110°C and 140°C for 6hrs.

$$T_g = T_g^0(°C) + A\,\frac{t^n}{B+t^n} \qquad\text{-------- (iii)}$$

Where, $T_o = T_g$ for no post curing

  t = Post curing time (hrs)

  A, B and n are constants

Table 2. Values of constants for 80, 110 and 140°C for equation (iii)

Temperature ($^{\circ}$C)	A	B	n
80	29.45	14.9	2.67
110	36.51	7.29	0.15
140	186.03	2.57	0.13

From table 2 it can be seen that the time coefficient (A) drastically increases with increase in curing temperature. 'A' is the dominating factor at lower time and hence at the earlier stage of curing time. The T_g is strongly dependent on 'A.' As at 140°C, the A value is quite high an instantaneous increase in T_g is noticed at small 't' values. The exponent (n) represents the dependency of T_g on time. The value of 'n' is quite high at 80°C, hence the T_g is strongly dependent on time. With increase in curing temperature, the 'n' value significantly reduces and at 140°C it achieves a value of 0.13. Hence at 140°C, T_g has a little dependency on time.
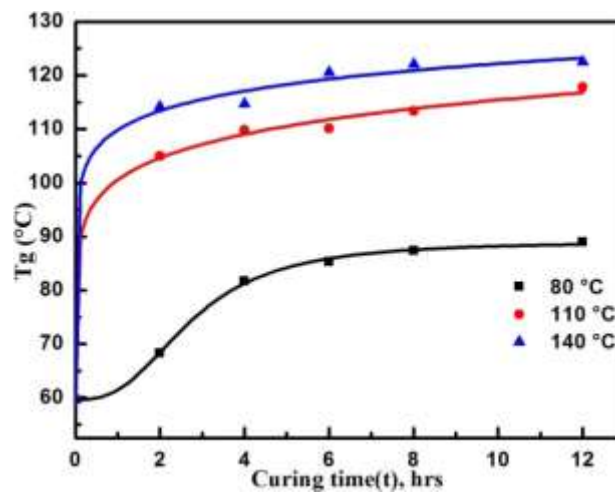

Figure 5. Variation in Tg with curing time at different curing temperatures

The figure 5 represents variation in T_g with curing time at different curing temperatures. At 80°C, initially the rate of increase in T_g for 2 hrs is higher as compared to other post curing time. Then the rate of increasing in T_g gradually slows down and after 6hrs the T_g get saturated. At high post curing temperatures i.e. 110°C and 140°C the rapid increase in T_g is observed for 2 hrs. After 2 hrs further exposing the samples for longer duration did not significantly altered the T_g and the T_g is almost saturated after 4hrs time for both 110°C and 140°C.

Figure 6(a) shows the SEM micrograph of fractured surface of a non-post cured GFRP specimen which was tested in 3-pont bend test. Polymer matrix without post curing is not sufficiently strong and under loading condition failure of composite primarily occurs due to the crushing of polymer matrix. Matrix crushing resulted in formation of small clusters of matrix which are adhered on the fibre surfaces as shown in figure 6(a). Whereas post curing of composite makes the polymer matrix significantly strong through the formation of well cross-linked polymer networks. The primary mode of failure in post cured GFRP is the failure at interface which leads to fibre/matrix debonding and further upon loading results in complete detachment of fibres from the matrix as shown in figure 6(b).
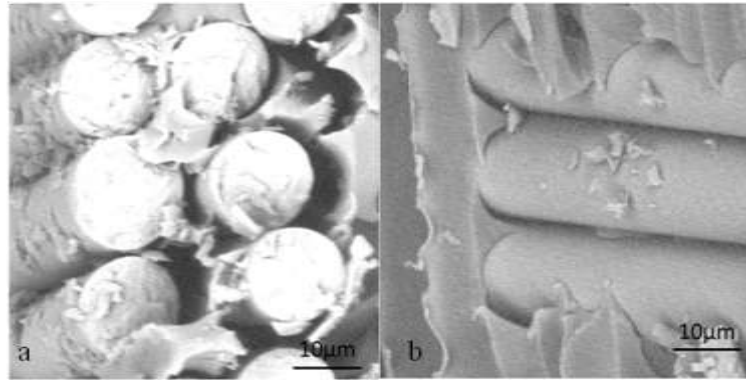
Figure 6. Scanning electron microscopy (SEM) images of fractured surface of glass fibre/epoxy composite a) without post curing. b) with post curing at 140°C for 6 hrs.

4. Conclusions

The following conclusions can be drawn from the present investigation

1. At 80°C temperature, no significant improvement in ILSS was noticed even after 12hrs of conditioning. The energy available at these post curing parameters may not be sufficient to further enhance the wettability at the fibre/matrix interface, which in turn reflects no improvement in ILSS.
2. At 110°C the ILSS value increases with time steadily at a very slower rate like mentioned as above equation (i).
3. At 140°C temperature a very drastic increment in ILSS value was observed at an earlier state. A linear trend is noticed as shown in equation (ii). This trend of increment is observed to be valid till a certain period of time i.e. 6hs after which the ILSS gets saturated.
4. High temperatures like 110°C and 140°C the energy received by the system is fairly high for activating the monomers to further cross-link.
5. From the present investigation it was observed that post curing at 140°C for 6 hrs gave better thermal and mechanical properties as compared to post curing at different temperatures and time periods.
6. The variation of T_g with time for different temperature is plotted and the governing mathematical expression is provided. The variation in T_g followed a trend as fitted with sigmoidal curve.

References

[1] Ray B C and Rathore D 2014 Durability and integrity studies of environmentally conditioned interfaces in fibrous polymeric composites: Critical concepts and comments *Adv. Colloid Interface Sci.* **209** 68–83
[2] Aruniit A, Kers J, Krumme A, Poltimäe T and Tall K 2012 Preliminary Study of the Influence of Post Curing Parameters to the Particle Reinforced Composite's Mechanical and Physical Properties *Mater. Sci.* **18** 256–61
[3] Furtos G, Silaghi-Dumitrescu L, Moldovan M, Baldea B, Trusca R and Prejmerean C 2012 Influence of filler/reinforcing agent and post-curing on the flexural properties of woven and unidirectional glass fiber-reinforced composites *J. Mater. Sci.* **47** 3305–14
[4] Stark W 2013 Investigation of the curing behaviour of carbon fibre epoxy prepreg by Dynamic Mechanical Analysis DMA *Polym. Test.* **32** 231–9