CHARACTERIZATION AND MODELING OF CREEP BEHAVIOR IN AMBIENT TEMPERATURE CURED THERMOSET RESIN

A Thesis in
Engineering Mechanics
by
Anurag Jaipuriar

© 2011 Anurag Jaipuriar

Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science

August 2011
The thesis of Anurag Jaipuriar was reviewed and approved* by the following:

Charles E. Bakis  
Distinguished Professor of Engineering Science and Mechanics  
Thesis Advisor

Maria Lopez de Murphy  
Associate Professor of Civil Engineering

Renata S. Engel  
Professor of Engineering Science and Mechanics  
Associate Dean for Academic Programs

Judith A. Todd  
P.B. Breneman Department Head Chair  
Professor of Engineering Science and Mechanics

*Signatures are on file in the Graduate School
ABSTRACT

Externally bonding fiber reinforced polymer (FRP) composites to existing structures as a method of increasing strength is a quick and convenient retrofitting technique for structurally deficient structures. FRP strengthening systems typically utilize an ambient cured epoxy resin as matrix as well as adhesive. Ambient cured epoxies may have a glass transition temperature ($T_g$) close to the service temperature. The $T_g$ being close to service temperature results in increased rate of physical aging which in turn results in the evolution of material properties. At temperatures close to $T_g$, creep deformation in the epoxy resin is also magnified. Hence it is important to characterize the $T_g$ and creep behavior in the constantly evolving ambient cured epoxy resin. Dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) were utilized to study the $T_g$ evolution with age of epoxy. For a 7-day-old epoxy the onset of glass transition was around 40°C. An increase in $T_g$ of almost 15°C was observed between a 7-day-old resin specimen and a specimen aged 100 days at room temperature, based on the dynamic storage modulus. The differences in various methods of assigning $T_g$ mechanical and thermal testing was also observed.

To gain understanding of the increase in $T_g$ with material age, cure kinetics and physical aging kinetics models for the epoxy resin were developed. Physical aging at ambient temperature was identified as the reason for the increase in $T_g$ of the resin. An “extent of aging” parameter was proposed to parameterize the evolution of epoxy resin towards equilibrium at the aging temperature. To characterize the creep response, tensile tests of plain epoxy coupons were done at ages of 7, 30 and 100 days at three different temperatures—22°C, 30°C and 35°C. As the specimen aged, it became stiffer and creep compliance and creep rate decreased dramatically for given testing temperatures. The knowledge of physical aging kinetics was utilized to link the mechanically observed creep behavior to “extent of aging” parameter. The novelty of this technique is in the ease with which aging can be characterized for a complex thermal history of polymer which governs its creep behavior. The advantage of using this technique over preceding
work to model non-isothermal aging is that creep response is not derived from parameters of a structural recovery model but a more tangible experimentally measured quantity. A MATLAB® based code was developed based on this technique to predict the creep behavior of resin aged at 22°C for a variable time and then subjected to creep loading at different temperatures. The predictions of the analytical model were in good agreement with the experimentally observed creep behavior for most of the cases, particularly in terms of creep rate at times greater than 50 hours.
TABLE OF CONTENTS

LIST OF FIGURES......................................................................................................................... vii

LIST OF TABLES.............................................................................................................................. x

ACKNOWLEDGEMENTS.................................................................................................................... xi

Chapter 1 Introduction ......................................................................................................................... 1
  1.1 Externally Bonded FRP reinforcement .................................................................................. 1
  1.2 Effect of Elevated Temperature and Sustained Loading ....................................................... 4
  1.3 Motivation and Research Objectives .................................................................................... 7

Chapter 2 Characterization of Glass Transition Temperature ............................................................ 8
  2.1 Introduction .............................................................................................................................. 8
  2.1.1 Assignment of $T_g$ using DMA ..................................................................................... 10
  2.1.2 Assignment of $T_g$ using DSC ...................................................................................... 11
  2.2 Experiments ............................................................................................................................ 14
    2.2.1 DMA Characterization of $T_g$ .................................................................................... 14
    2.2.2 DSC Characterization of $T_g$ ..................................................................................... 19
  2.3 Results and Discussion ............................................................................................................ 20
    2.3.1 DMA Results ............................................................................................................... 20
    2.3.2 DSC Results ................................................................................................................. 28
  2.4 Conclusion ............................................................................................................................... 30

Chapter 3 Investigation of Cure Kinetics and Physical Aging Kinetics in Epoxy Resin .................... 32
  3.1 Introduction .............................................................................................................................. 32
  3.1.1 Literature Review on Cure Kinetics of Epoxy Resin ....................................................... 32
  3.1.2 Literature Review on Physical Aging Kinetics of Epoxy Resin ....................................... 34
  3.2 Experimental Program .......................................................................................................... 40
    3.2.1 Chemical Cure Kinetics .............................................................................................. 40
    3.2.2 Physical Aging Kinetics .............................................................................................. 41
  3.3 Results and Discussion .......................................................................................................... 41
    3.3.1 Model for Prediction of Degree of Cure ($\alpha$) ............................................................ 41
    3.3.2 Physical Aging Evolution Model .................................................................................. 48

Chapter 4 Prediction of Tensile Creep Behavior in Epoxy Resin ....................................................... 53
  4.1 Introduction .............................................................................................................................. 53
  4.2 Objectives ............................................................................................................................... 54
  4.3 Literature Review .................................................................................................................... 54
  4.4 Experiment .............................................................................................................................. 62
    4.4.1 Tensile Creep Test Specimen Preparation .................................................................... 62
    4.4.2 Creep Test Set-up .......................................................................................................... 63
    4.3.3 Creep Test Program ...................................................................................................... 66
  4.4 Creep Test Results ................................................................................................................... 68
LIST OF FIGURES

Figure 1-1: Installation of flexural FRP reinforcement using hand layup technique ............... 2
Figure 1-2: Structure of DGEBA resin and isophorone diamine hardener .............................. 3
Figure 1-3: Schematic of load transfer in externally bonded FRP ........................................... 4
Figure 1-4: Sustained loading setup (a) and debonding failure mode (b) for plain concrete beams with externally bonded CFRP reinforcement [9] .................................................. 6
Figure 2-1: Relationship between storage $E', E''$ and $E^*$ .................................................. 11
Figure 2-2: Typical DSC scan .................................................................................................. 12
Figure 2-3: Schematic representation of heat flux DSC .......................................................... 13
Figure 2-4: Schematic representation of a power compensated DSC ...................................... 13
Figure 2-5: Steel mold for thin film specimen ......................................................................... 15
Figure 2-6: Schematic diagram of Teflon mold for film specimen .......................................... 16
Figure 2-7: DMA equipment and thin film resin specimen gripped in the tension film clamp ................................................................................................................................ 18
Figure 2-8: DSC equipment and DSC cell close-up view ....................................................... 20
Figure 2-9: Typical repeated scans of (a) storage modulus, (b) loss modulus and Tan $\delta$ for a 7-day-old resin specimen ......................................................................................... 21
Figure 2-10: Summary of first run DMA $T_g$ data for epoxy cured for 7, 30 and 100 days at room temperature, from batches A, B, and C. .............................................................. 22
Figure 2-11: Comparison of $T_g$ for soaked and unhydrated specimens at different ages using storage modulus (SM), loss modulus (LM) and Tan $\delta$(TD) .............................................. 26
Figure 2-12: Raw DMA data for a typical specimen soaked for 93 days ................................ 28
Figure 2-13: Two consecutive DSC scans on a 7-day-old specimen from Batch B’ ................ 29
Figure 2-14: Summary of DSC $T_g$ data for epoxy cured for various numbers of days at room temperature, from batches A’, B’, and C’ ................................................................. 30
Figure 2-15: Enhancement in $T_g$ using DMP 30 accelerator with generic resin mixture: (a) EPON 862/IPDA; (b) EPON 862/IPDA/DMP 30. ................................................................. 31
Figure 3-1: (a) Specific volume variation with temperature and the deviation of specific volume from equilibrium below $T_g$, (b) Variation of molecular mobility with specific volume ............... 35
Figure 3-2: Evolution of enthalpy towards equilibrium (Stage A: Un-aged specimen, Stage B: Partially aged specimen) and heat capacity curves at the two stages of aging [26] ........................................................................................................................ 37

Figure 3-3: Endothermic DSC peaks for fully cured Epon 828/MDA samples physically aged at 130°C for aging times up to 648 hours (reproduced from [22]) ...................................................... 38

Figure 3-4: Graphical assignment of fictive temperature ($T_f$) (reproduced from [26]) .............. 39

Figure 3-5: DSC scans and heat of reaction value of freshly mixed resin at (a) 3°C/min (b) 5°C/min (c) 8°C/min and (d) 10°C/min. ................................................................................................. 42

Figure 3-6: Degree of cure versus time at different heating rates ................................................. 43

Figure 3-7: Isoconversion curves of curing time and heating rate from DSC experimental data ........................................................................................................................................ 44

Figure 3-8: Dependence of fit parameters, $P$ and $Q$, on degree of cure ($\alpha$) ......................... 45

Figure 3-9: Isoconversion map for MBrace saturant resin ........................................................ 46

Figure 3-10 Residual enthalpy of a 7-day-old epoxy sample cured at 22°C temperature. ...... 47

Figure 3-11: Effect of 40°C exposure on $T_g$ and residual cure enthalpy for resin aged for 10 days at room temperature ............................................................................................................. 48

Figure 3-12: Evolution of relaxation enthalpy for resin cured and ............................................. 49

Figure 3-13: $T_g$ evolution with aging at different temperatures ................................................. 50

Figure 4-1: Typical creep response of viscoelastic material ...................................................... 55

Figure 4-2: Time-temperature superposition to construct creep master curve ......................... 58

Figure 4-3: Time aging time superposition to construct creep master creep compliance curve [24]. ................................................................................................................................. 60

Figure 4-4 Schematic showing temperature up-jump before creep testing of specimen to simulate nonisothermal aging (reproduced from [39]) .............................................................. 61

Figure 4-5 Sheet mold assembly .............................................................................................. 63

Figure 4-6 Lever arm creep frame ........................................................................................... 64

Figure 4-7: Wedge grip assembly with extensometers mounted specimen (left) and custom-made clamp grip assembly (right). ......................................................................................... 66

Figure 4-8: Summary of creep compliance versus time at 22°C ............................................. 69

Figure 4-9: Summary of creep compliance versus time at 30°C ............................................. 70
Figure 4-10: Summary of creep compliance versus time at 35°C ........................................... 70

Figure 4-11: Representative creep compliance curves for 7-day-old specimens tested at 22°C, 30°C and 35°C. ...................................................................................................... 74

Figure 4-12: Representative creep compliance curves for 30-day-old specimens tested at 22°C, 30°C and 35°C ....................................................................................................... 75

Figure 4-13: Representative creep compliance curves for 100-day-old specimens tested at 22°C, 30°C and 35°C ....................................................................................................... 75

Figure 4-14: Best-fit functions for elastic modulus of epoxy resin at various ages and temperatures ..................................................................................................................... 77

Figure 4-15: $T_g$ evolution at different aging temperatures. ...................................................... 79

Figure 4-16: Piecewise power law fitted to average representative creep compliance curve for 7-day-old specimen tested at 30°C ................................................................... 80

Figure 4-17: Creep compliance curves of 7-day-old epoxy resin tested at different temperatures with points of $\beta=0.965$ marked .................................................................. 83

Figure 4-18: Graph for determination of activation energy at various $\beta$ ............................. 84

Figure 4-19: Variation of $(Q/R)$ with “extent of aging” parameter $\beta$ ............................... 85

Figure 4-20: Creep prediction flowchart .................................................................................. 87

Figure 4-21: Model prediction for creep of 30D-22°C specimen ............................................ 88

Figure 4-22: Model prediction for creep of 30D-30°C specimen ............................................ 89

Figure 4-23: Model prediction for creep of 30D-35°C specimen ............................................ 89

Figure 4-24: Model prediction for creep of 100D-22°C specimen ........................................ 90

Figure 4-25: Model prediction for creep of 100D-30°C specimen ........................................ 90

Figure 4-26: Model prediction for creep of 100D-35°C specimen ........................................ 91

Figure B-1: Master creep curve for 7D-22°C-2 specimen. ...................................................... 127

Figure B-2: Logarithm of aging time and horizontal shift showing the constant rate of increase of shift factor ............................................................................................................. 128

Figure D-1: First DSC scan showing the presence of physical aging in resin ....................... 134

Figure D-2: Second DSC scan after exposing the specimen to temperature above its $T_g$ ................................................................................................................................. 134
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>Dimensions of individual DMA specimens</td>
<td>17</td>
</tr>
<tr>
<td>2-2</td>
<td>$T_g$ assigned using storage modulus ($T_{gSM}$)</td>
<td>23</td>
</tr>
<tr>
<td>2-3</td>
<td>$T_g$ assigned using loss modulus ($T_{gLM}$)</td>
<td>23</td>
</tr>
<tr>
<td>2-4</td>
<td>$T_g$ assigned using Tan $\delta$ ($T_{gTD}$)</td>
<td>24</td>
</tr>
<tr>
<td>2-5</td>
<td>Moisture content and first-run $T_g$ for saturated specimens</td>
<td>26</td>
</tr>
<tr>
<td>4-1</td>
<td>Phenomenological models for modeling creep behavior</td>
<td>56</td>
</tr>
<tr>
<td>4-2</td>
<td>Number of specimens tested for each combination of age (prior to test) and temperature during test</td>
<td>67</td>
</tr>
<tr>
<td>4-3</td>
<td>Summary of creep specimen dimensions and test stress levels</td>
<td>68</td>
</tr>
<tr>
<td>4-4</td>
<td>Average representative creep compliance functions for various test conditions</td>
<td>72</td>
</tr>
<tr>
<td>4-5</td>
<td>Elastic modulus of epoxy resin at different ages and test temperatures</td>
<td>76</td>
</tr>
<tr>
<td>4-6</td>
<td>Fitted creep law parameters $A$ and $b$ for different ranges of creep time and corresponding “extent of aging” parameter at 30°C</td>
<td>81</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

I would like to express my sincere thanks to my advisor, Dr. C.E. Bakis for giving me an opportunity to work on this thesis topic. As an individual, I have learnt a lot about discipline, work ethics and passion for scientific research from him. I would also like to thank Dr. Lopez for her constant guidance and encouragement during the research work. Being an interdisciplinary research topic, her inputs were very valuable in completion of this thesis. I would like to acknowledge the financial support of the National Science Foundation (grant CMMI-0826461), the Penn State College of Engineering and the Department of Engineering Science and Mechanics. The help and guidance of Dr. Brown and Dr. Hamilton by providing access to testing facilities in their laboratory deserves to be acknowledged.

I would like to thank my friends and colleagues in my research group for their help and support especially Jeff Flood, Yoseok Jeong and Ye Zhu. I would also like to thank my parents and family members for their love and blessings during my stay at Penn State.

I am thankful to the faculty and staff members of the Engineering Science and Mechanics Department, especially Mr. Ardell W. Hosterman and Mr. Scott Kralik, for helping me troubleshoot any technical problem in the laboratory.
Chapter 1

Introduction

Traditionally, civil infrastructures have been made out of masonry, concrete, timber, and steel. With continuous research and development in the application of fiber reinforced polymer (FRP) as a construction material, FRP has gained acceptance as a viable alternative. FRP material is known for its high strength-to-weight ratio, high stiffness and good corrosion resistance. Thus, the use of FRP enables reduction of dead weight of the structure and extends the life of the structure. One of the applications of FRP is as externally bonded reinforcement to masonry, concrete, timber, and steel structures. This application is becoming increasingly popular to repair and strengthen a structure already in-service.

1.1 Externally Bonded FRP Reinforcement

The application of FRP as externally bonded reinforcement can be dated back to early 1980s. A good survey of the developments in the use of FRP reinforcement for civil infrastructure can be found in literature [1-3]. Adhesively bonded precured FRP laminates were the first kind of FRP strengthening system for concrete structures studied by Urs Meier and his team at the Swiss Federal Lab for Material Testing and Research (EMPA). The use of FRP is advantageous as it requires less installation time and labor in comparison to conventional methods like use of steel plates or jackets for strengthening a structure. The externally bonded reinforcement is installed either by adhering or mechanically fastening pre-cured FRP laminate or by actually applying and curing the fabric and resin system in-situ by the hand layup technique. Hand lay-up technique involves applying a thin layer of resin on the substrate and then installing layers of fabric,
saturated with resin on the substrate as shown in Figure 1-1. After curing, the fabric adheres to the substrate, taking the form of the substrate on which it is laid. Externally bonded reinforcement can be used for increasing load carrying capacity of structures in flexure, shear and also compression when used to confine the structure.

Near surface mounting (NSM) is a relatively new strengthening technique in which precured FRP bars or strips is adhesively bonded to grooves cut into the concrete substrate. This technique helps in protecting the bonded FRP from collision, high temperature and UV degradation damage. The debonding strength is higher in comparison to externally bonded FRP due to increased bonded area per unit length of reinforcement. However the NSM strengthening technique requires preparation time and cutting of concrete cover may not always be feasible.

FRP consists of continuous fibers and polymeric resin matrix. The fiber used can be glass carbon, aramid or high strength steel fiber. For externally bonded repair the fibers are woven or stitched together to produce “fabric” which is saturated by the resin. The resin used can be an
epoxy resin, polyester resin or vinyl ester resin. Epoxy resins have better mechanical properties than other two and are most commonly used. Fiber reinforced cementitious grout has also been utilized as externally bonded strengthening system [4-5]. The use of cementitious grout as matrix improves fire resistance of structure and resolves the problem of induced thermal stress between FRP and concrete substrate.

Epoxy resin is a copolymer of a monomer with an epoxide functional group known as “epoxide” and a monomer with an amine functional group known as “hardener.” The resin is generally based on diglycidal ether of bisphenol A (DGEBA). The variation in hardener’s chemical formulation varies the crosslink density and the resulting properties of the epoxy polymer. Figure 1-2 shows the structure of a DGEBA based resin and a cycloaliphatic amine, isophorone diamine (IPDA), which can be used as hardener. The reaction between resin and hardener produces a network type molecular configuration. The crosslink density also depends upon the extent of reaction between resin and hardener.

![DGEBA](image)

**Figure 1-2: Structure of DGEBA resin and isophorone diamine hardener**

The cured FRP laminate and the structure behave in a composite fashion. The load on the structure is transferred to the FRP laminate through shear stress at the FRP-resin-concrete
interface. The shear stress at discontinuities in the substrate (e.g., concrete crack) or FRP (e.g., termination point) is relatively high due to stress concentration and decreases almost exponentially away from the discontinuity, as shown in Figure 1-3 for the FRP termination point. This high shear stress can result in debonding of FRP from the substrate, which is the most common mode of failure of externally bonded FRP systems [2].

![Figure 1-3: Schematic of load transfer in externally bonded FRP](image)

1.2 Effect of Elevated Temperature and Sustained Loading

The FRP external strengthening system consists of glass or carbon fiber and, typically, epoxy resin as the matrix and adhesive. The system is most often installed and cured at an ambient temperature, although heating systems such as electrical heaters, infrared heaters and heat blankets have been attempted with much higher installation cost. Heating devices which utilizes electrical conductivity of carbon fibers to heat cure the CFRP laminate by passing electric current have also been developed but are not commonly used [6]. Cooler temperatures slow the curing process, while warmer temperatures accelerate it. The desired result of curing is a polymer with rigid, or glassy, characteristics throughout the expected service temperature range. At
sufficiently high temperatures, polymers lose their desired glassy characteristic and behave as rubbery materials [7]. This phenomenon is known as the glassy-rubbery transition. The transition takes place over a range of 5-10°C. A particular temperature in this range is assigned as the glass transition temperature \( T_g \). As epoxy resins used in FRP external strengthening applications are typically cured at room temperature the extent of chemical cure is less than 100% [8]. The glass transition temperature, which is dependent of the extent of chemical cure and the crosslink density in the resin system, is generally close to the service temperature when the service temperature is the only source of thermal energy for curing. At temperatures close to the \( T_g \), polymeric materials also exhibit considerable time dependent deformation under sustained loading, also known as creep deformation. Hence to predict the effect of creep in FRP strengthened concrete structures it is important to understand the combined effect of temperature and sustained mechanical loading on the polymeric resin system.

The effect of elevated temperature on the bond properties of FRP externally bonded on concrete structures has been reported in only a few publications [9][10][11]. Bakis [9] discussed the importance of \( T_g \) in relation to elevated temperature capability and safety of structures. He also discussed the various methods of assigning \( T_g \) and the variability in the assigned value of glass transition temperature. Leone et al. [10] describe an experimental investigation carried out on FRP strengthened concrete double-lap shear specimens tested at temperatures near and above \( T_g \). The maximum bond strength at the FRP-concrete interface decreased with increasing test temperature. In specimens tested for bond strength at a temperature of \( T_g +20°C \), loss of adhesion at the FRP epoxy concrete interface and debonding of FRP from the substrate was observed. Klamer et al. [11] also evaluated strength of double-lap shear specimens and reported an increase in failure strength with increase in test temperature below \( T_g \). At elevated temperature below \( T_g \)
the failure took place in the concrete near the interface. For temperatures above \( T_g \), a decrease in ultimate load was observed and failure took place exactly at the FRP-concrete interface.

The importance of combined sustained load and elevated temperature is underlined considering results reported by Bakis [9]. Notched, plain concrete beams with externally bonded carbon FRP (CFRP) tensile reinforcement were placed under a constant flexural load using springs, as shown in Figure 1-4a, so that the fibers were under a tensile stress of about 50% of ultimate. Following 1 to 6 days of exposure in the ambient summer weather (~40°C surface temperature and ~80% relative humidity), the CFRP reinforcement catastrophically debonded at the epoxy/concrete interface, as seen in Figure 1-4b. The reduction in physical properties of epoxy resins over a temperature range associated with glass transition temperature, \( T_g \), was suspected to be the cause of the loss of bond strength. It is therefore critical to understand the bond behavior FRP bonded to concrete at elevated temperatures and sustained loads.

Figure 1-4: Sustained loading setup (a) and debonding failure mode (b) for plain concrete beams with externally bonded CFRP reinforcement [9]
1.3 Motivation and Research Objectives

Detailed design guidelines for design of new and repair of old concrete structures with externally bonded FRP have been developed. American Concrete Institute’s ACI 440.2R [12] and European task group fib (International Federation for Structural Concrete) 9.3’s Bulletin 14 [6] are two of the most widely used design guidelines for externally bonded FRP reinforcement. The design guidelines lack substantial coverage of long term durability and effect of creep and elevated temperature on FRP external strengthening systems.

The major objective of this investigation is to develop a model to predict creep in epoxy resin used in FRP strengthening systems for a given mechanical and thermal loading history of the epoxy resin. Such a model, when incorporated in a numerical code, can be used to predict the long term response of structure subjected to sustained loading. It will be helpful in studying the effect of creep at elevated temperature on the residual strength of FRP strengthened structures. The investigation is focused on a commercially available epoxy resin system marketed to be used as a fiber saturant and adhesive for installing externally bonded FRP systems onto concrete, masonry, and timber. As the temperature capability of the composite repair system is dependent on the glass transition temperature of the resin system used, the $T_g$ of the resin is characterized at ages of 7, 30 and 100 days. The $T_g$ is characterized using two techniques—dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). DSC is used to further study the evolution of $T_g$ and physical and chemical aging kinetics in the epoxy resin used in the investigation. Tensile creep behavior of the plain resin is studied at different temperatures and ages. The observed creep behavior along with the knowledge of aging kinetics is used to develop a predictive model for evaluating creep behavior in the resin.
Chapter 2

Characterization of Glass Transition Temperature

2.1 Introduction

Glass transition is an important phenomenon associated with viscoelastic materials like polymeric resins. According to ASTM E1142 [13]—standard terminology relating to thermophysical properties—it is defined as “the reversible change in an amorphous material or in amorphous regions of a partially crystalline material, from (or to) a viscous or rubbery condition to (or from) a hard and relatively brittle one.” The glass transition is thermodynamically classified as a second order transition or alpha transition in which there is no abrupt change in volume of the material undergoing transition, unlike a melting point. As a material is heated through the glass transition temperature, it exhibits large scale segmental motion of polymeric chains. At temperatures lower than glass transition temperature polymers can exhibit localized motion of polymer chains or side groups and are classified as sub-\( T_g \) transitions (beta and gamma transition). The glass transition temperature of an epoxy polymer depends on the chemical reactivity of the epoxide amine reaction at the temperature of cure. It is also dependent on the time for cure. Increased cure time and temperature both increase the degree of cure, which in-turn increases the glass transition temperature of epoxy. The present investigation focuses on ambient temperature cured epoxy resin. As the epoxide (resin) and amine (hardener) are mixed, the chemical reaction initiates and degree of cure starts to advance. When the degree of cure advances to a stage where \( T_g \) starts exceeding the cure temperature, the epoxy resin vitrifies.
Vitrification of epoxy resin reduces the mobility of chains and reduces the rate of chemical reaction which effects further advance of degree of cure and increasing of the $T_g$. Thus, with ambient temperature cure it is difficult to achieve the maximum achievable $T_g$ of the resin system. For epoxy cured at ambient temperature, the $T_g$ is also affected by the phenomenon of physical aging or structural relaxation.

The glass transition occurs in a narrow temperature range. In general, a temperature point within the narrow temperature range is used to specify the glass transition temperature. But, since the glass transition phenomenon may itself occur over a range of several degrees, assigning a singular temperature as $T_g$ results in ambiguity. The glass transition phenomenon is observed by measuring electrical, mechanical, thermal, or other physical properties which change significantly over the transition temperature range. For example DSC (differential scanning calorimetry) assigns $T_g$ based on changes in specific heat capacity, TMA (thermo-mechanical analysis) assigns $T_g$ based on changes in coefficient of thermal expansion, and DMA (dynamic mechanical analysis) assigns $T_g$ by measuring changes in the dynamic stress-strain behavior. The $T_g$ values assigned using these different methods often differ from each other significantly and are furthermore dependent on the procedural details within any one method.

The objective of the portion of the investigation described in this chapter is to assign glass transition temperature to the resin and also study the evolution of $T_g$ with age of resin. The investigation also compares different methods of assignment of $T_g$. Another objective of this part of the investigation is to study the effect of moisture on the $T_g$. 
2.1.1 Assignment of $T_g$ using DMA

As discussed above, DMA is one of the well-known experimental techniques for determining the $T_g$ of polymeric materials. DMA involves applying a stress (or strain) varying sinusoidally in time and measuring the corresponding sinusoidal strain (or stress) magnitude and phase shift. Time, temperature and loading frequency are the test parameters that can be varied during DMA testing. ASTM E1640 [13] describes a standard test method for the assignment of $T_g$ by DMA for thermoplastic and thermosetting polymers and partially crystalline materials. In the present investigation, fixed strain amplitude and frequency were applied as the temperature was varied through the $T_g$. Due to the viscoelastic nature of the material, a phase difference exists between the strain and stress in the specimen. The steady-state stress to strain ratio, $E^*$, is therefore a complex quantity having in-phase and out-of-phase components,

\[ E^* = E' + iE'' \tag{2-1} \]

where $E'$ is the ratio of stress to in-phase strain and $E''$ is the ratio of stress to $90^\circ$ out-of-phase strain. $E'$ is also known as the storage modulus as it relates to mechanical energy stored in the material, whereas $E''$ relates to viscous energy dissipated and is therefore known as the loss modulus. The schematic depicted in Figure 2-1 shows the phasor relationships among $E'$, $E''$ and $E^*$. 


The \( T_g \) of a material can be assigned by the onset of the rapid loss of storage modulus with increased temperature and by the peaking of the loss modulus over the glass transition temperature range. The loss modulus can be determined by Equation 2-2, where Tan \( \delta \) is known as the *loss factor* and \( \delta \) is the *phase angle* between the stress and strain.

\[
E'' = E' \tan\delta
\]  

(2-2)

The peak of a plot of Tan \( \delta \) versus temperature can also be used to assign \( T_g \). Thus, using a DMA apparatus, one can assign the \( T_g \) based on a plot of the storage modulus, loss modulus, or Tan \( \delta \) versus temperature.

### 2.1.2 Assignment of \( T_g \) using DSC

Differential scanning calorimetry is a thermoanalytical technique which accurately measures the heat inflow or outflow from a specimen when exposed to a controlled thermal
condition [14]. DSC is typically used to measure transition temperatures and heat of transition. When a polymer undergoes a glass transition, the heat capacity of the specimen undergoes a step change which is used to assign \( T_g \). Figure 2-2 shows a typical DSC scan showing the step change in heat flow as the experimental sample undergoes glass transition.

Differential scanning calorimeters can be classified into two classes depending on their working principle: power compensated DSC and heat flux DSC. The heat flux DSC consists of sample and reference pan in the same furnace (as shown in Figure 2-3). The sample pan holds the sample to be tested whereas the reference pan is empty. The sample and reference pan are identical in all other respects. As the furnace is heated, the temperature difference between the two pans is measured by thermocouples attached to the bases below each pan. The temperature difference is converted into heat flow in or out of the sample pan using thermal equivalent resistance of the base plate.
The power compensated DSC consists of two separate furnaces, each with its individual heater and temperature sensor (as shown in Figure 2-4). The basic principle of operation of a power compensated DSC is maintaining a “thermal null” system. As both the pans are heated at the same rate, the amount of heat absorbed or released by the sample is reflected in the difference in energy provided to the two pans.

DSC equipment should be calibrated using high purity substance with known thermal properties. The procedures and guidelines for calibration have been discussed in-detail elsewhere [14]. Two types of calibration are done on the DSC equipment—temperature calibration and
caloric calibration. In the present investigation, high purity indium was used to check both temperature and caloric calibration.

2.2 Experiments

A commercially available resin system used for saturating FRP strengthening system was chosen for characterizing glass transition temperature using DMA and DSC. The product is marketed by BASF chemicals (www.basf.com) and is sold under the brand name “MBrace Saturant.” The resin is a two part epoxy resin with Bisphenol-A epoxy as the major constituent of the “resin part” and isophoronediamine as the major constituent of the “hardener” part. The application of this resin involves curing it at ambient temperature. Hence it is of interest to assign the $T_g$ and investigate the evolution of $T_g$ for the resin system with age.

2.2.1 DMA Characterization of $T_g$

DMA testing was done on a TA Instruments Q800 dynamic mechanical analyzer in the tensile mode. The $T_g$ test sequence was determined according to ASTM E1640 (2004). The glass transition temperature was assigned using each of the three methods as discussed earlier:

- Onset of decrease of the storage modulus, $E'$, versus temperature plot—i.e., the midpoint of the temperature range over which the rate of decrease of $E'$ with increasing temperature dramatically increases;
- Peak of the loss modulus, $E''$, versus temperature plot;
- Peak of the Tan $\delta$ versus temperature plot.
The resin was mixed in the proportion mentioned in manufacturer’s technical data sheet. Upon completing the mixing procedure, the material was immediately placed in a vacuum chamber and degassed in order to minimize the presence of air voids in the material. Degassing of resin was an important aspect in specimen preparation since the specimen thickness was only ~0.3 mm and any air voids could change the specimen cross-sectional properties significantly. The resin was molded between two steel plates held together by three layers of 0.1-mm-thick double sided tape (Figure 2-5). These plates were submerged inside a Teflon container filled with the material (Figure 2-6) and then degassed in a vacuum chamber at ambient temperature for at least 15 minutes. Silicone based mold release agent manufactured by Huron technologies was used to prevent epoxy from adhering to the aluminum surface and to aid in easy removal of cured sheets from the mold.

Figure 2-5: Steel mold for thin film specimen
To ensure some degree of assessment of batch-to-batch variability, three different batches of resin were mixed and molded into thin films. One specimen was tested from each batch at each target age. Films were allowed to cure for 7 days in the air-conditioned laboratory environment before demolding them. Demolded films were cut into specimens of approximately 30 mm in length, 5 mm in width, and 0.3 mm in thickness using a utility knife. The specimens and the unused sheet of resin were stored in a desiccator with anhydrous calcium sulfate based desiccant. Dimensions of individual specimens are tabulated in Table 2-1. The number in the specimen nomenclature indicates the age of the specimen in days and the letter indicates the batch identifier. For example, for the specimen named 30B, 30 represent age in days and B indicates the batch name. Specimens were tested at the ages of 7, 30 and 100 days (130 days in one of the batches).
Table 2-1: Dimensions of individual DMA specimens

<table>
<thead>
<tr>
<th>Specimen Name</th>
<th>Width (mm)</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7A</td>
<td>5.35</td>
<td>0.28</td>
</tr>
<tr>
<td>7B</td>
<td>4.79</td>
<td>0.27</td>
</tr>
<tr>
<td>7C</td>
<td>5.98</td>
<td>0.35</td>
</tr>
<tr>
<td>30A</td>
<td>4.3</td>
<td>0.24</td>
</tr>
<tr>
<td>30A</td>
<td>4.68</td>
<td>0.33</td>
</tr>
<tr>
<td>100A</td>
<td>5.92</td>
<td>0.28</td>
</tr>
<tr>
<td>100B</td>
<td>5.1</td>
<td>0.26</td>
</tr>
<tr>
<td>130C</td>
<td>5.03</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Specimen size is very important in testing material properties in the temperature-controlled furnace used in the DMA. The temperature of a thick specimen may lag behind the furnace temperature resulting in inaccurate measurement of mechanical properties with varying temperature. Thinner specimens allow for less temperature variation between the specimen and the point in the furnace where the feedback thermocouple is located.

The TA Instruments Q800 dynamic mechanical analyzer used in the present investigation is a non-contact, linear drive motor device with optical encoding for strain detection. The DMA is designed to take precise stress/strain measurements in a broad range of temperatures (-150 – 600°C). The device, as shown in Figure 2-7, has a furnace which allows the user to control environmental conditions and has various clamp types for different testing needs. The present tests have been done using tension clamps (Figure 2-7) and laboratory air environment inside the test chamber. Heating elements and liquid nitrogen were used to carry out rapid temperature changes. Due to the precision of the instrument, routine calibration needed to be performed before each test.
The $T_g$ test sequence was determined according to ASTM E1640 (2004) [13]. The tests were run using a constant maximum strain excursion of 0.05% and a frequency of 5 Hz. After DMA calibration, the following test sequence was followed.

Upon closing the furnace, temperature was equilibrated at -50°C and then held at constant temperature for 10 minutes. Temperature decreases were done at uncontrolled rates. No data was collected during this time period. Data storage then began and the temperature was ramped up at a rate of 3°C per minute until 120°C was reached. Data storage was then turned off. This cycle was repeated for three or six cycles per specimen.

A limited investigation of the effect of moisture on $T_g$ of epoxy was also carried out. Thin film specimens of average thickness 0.2-0.3 mm were molded and cured at room temperature for 7 days. After 7 days of curing, DMA specimens were immersed in de-ionized water at room temperature. Three batches of resin, namely $A_h$, $B_h$, $C_h$ were mixed and molded into film
specimen. A saturation moisture content of approximately 2.5% by weight was attained after 3 days in water. DMA scans, following the same test sequence as mentioned above, were done at ages of 30 days (23 days in water) and 100 days (93 days in water). Specimens were removed from the water and then wiped with paper towel to remove excess water from surface before gripping them in the DMA apparatus.

2.2.2 DSC Characterization of $T_g$

DSC tests were utilized to study the glass transition temperature. A TA Instruments Q100 DSC—a heat flux type DSC—was used in the present investigation. ASTM D3418-08 [15] was followed to assign the $T_g$. A sample mass of about 5 mg was used in each scan. Large volume stainless steel pans of 60 µL capacity manufactured by Perkin Elmer with a lid and rubber seal capable of sustaining high internal pressure were used in the scans to prevent any leakage of volatiles. The steel pans are placed over two circular raised pedestals as shown in Figure 2-8. Scans were done at 3°C/min from 0°C to 250°C after equilibrating the samples at 0°C in a nitrogen gas environment. In a few cases, the specimen was exposed to two consecutive heat-cool cycles. Heating was done at 3°C/min from 0°C to 250°C and cooling was done at 10°C/min from 250°C back to 0°C. To account for asymmetry in the measuring system, DSC scans with two empty pans were run to obtain what is known as the “zero line.” The zero line was subtracted from the scan data to obtain the actual heat flow to and from the test sample. DSC scans were done for three different batches ($A'$, $B'$, and $C'$) at age of 7, 30 and 100 days. These batches primed since they are not the same batches used in the DMA tests.
2.3 Results and Discussion

2.3.1 DMA Results

Glass transition temperature was assigned using the three different techniques as discussed in Section 2.1.1. Typical plot of variation of storage modulus ($E'$), loss modulus ($E''$) and Tan $\delta$ with temperature has been depicted in Fig. 2-5(a), (b) and (c) respectively. The assigned $T_g$ values for each sequential run number (e.g., Run 1 = $T_g$R1, etc.) are indicated in each DMA scan.
It can be seen that \( T_g \) increases with each thermal sweep cycle. This could be due to “post-curing” of the resin. As the specimen is heated above \( T_g \) molecular chains regain their mobility and unreacted epoxide and amine can undergo chemical reaction improving the crosslink density and hence increasing the \( T_g \) in next run. This also supports the argument that ambient temperature cured epoxy is not 100% chemically cured. For few of the DMA scans six consecutive scans were done quantify the maximum attainable \( T_g \). The storage modulus, loss
modulus and Tan δ for all DMA scans have been included in Appendix A. The summary of glass transition temperature assigned using three different methods at different ages—7, 30 and 100 days for the first run has been shown in Figure 2-10. For one particular batch specimen were tested at age of 130 days. The $T_g$ value assigned for all specimens in different runs using storage modulus, loss modulus and Tan δ have been tabulated in Tables 2-2, 2-3 and 2-4. Also included in the tables are the actual ages of the specimens when tested (as part of the specimen name).

![Figure 2-10: Summary of first run DMA $T_g$ data for epoxy cured for 7, 30 and 100 days at room temperature, from batches A, B, and C.](image-url)
Table 2-2: $T_g$ assigned using storage modulus ($T_{gSM}$)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$T_{gSM}$ (°C)</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>R4</th>
<th>R5</th>
<th>R6</th>
</tr>
</thead>
<tbody>
<tr>
<td>7A</td>
<td>42</td>
<td>50</td>
<td>61</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>7B</td>
<td>43</td>
<td>50</td>
<td>59</td>
<td>62</td>
<td>63</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>7C</td>
<td>36</td>
<td>46</td>
<td>57</td>
<td>58</td>
<td>65</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Average at 7 days</td>
<td>40</td>
<td>49</td>
<td>59</td>
<td>60</td>
<td>64</td>
<td>64</td>
</tr>
<tr>
<td>30A</td>
<td>51</td>
<td>66</td>
<td>63</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>30B</td>
<td>48</td>
<td>51</td>
<td>59</td>
<td>60</td>
<td>65</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>30C</td>
<td>48</td>
<td>53</td>
<td>59</td>
<td>63</td>
<td>64</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Average at 30 days</td>
<td>49</td>
<td>57</td>
<td>60</td>
<td>61</td>
<td>64</td>
<td>65</td>
</tr>
<tr>
<td>100A</td>
<td>59</td>
<td>57</td>
<td>62</td>
<td>64</td>
<td>67</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>100B</td>
<td>52</td>
<td>55</td>
<td>60</td>
<td>64</td>
<td>65</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Average at 100 days</td>
<td>55</td>
<td>56</td>
<td>61</td>
<td>64</td>
<td>66</td>
<td>66</td>
</tr>
<tr>
<td>130C</td>
<td>50</td>
<td>54</td>
<td>59</td>
<td>63</td>
<td>65</td>
<td>66</td>
<td></td>
</tr>
</tbody>
</table>

Table 2-3: $T_g$ assigned using loss modulus ($T_{gL,M}$)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$T_{gL,M}$ (°C)</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>R4</th>
<th>R5</th>
<th>R6</th>
</tr>
</thead>
<tbody>
<tr>
<td>7A</td>
<td>47</td>
<td>65</td>
<td>74</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>7B</td>
<td>49</td>
<td>67</td>
<td>76</td>
<td>79</td>
<td>82</td>
<td>83</td>
<td>83</td>
</tr>
<tr>
<td>7C</td>
<td>44</td>
<td>66</td>
<td>74</td>
<td>78</td>
<td>79</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>Average at 7 days</td>
<td>47</td>
<td>66</td>
<td>75</td>
<td>78</td>
<td>80</td>
<td>81</td>
</tr>
<tr>
<td>30A</td>
<td>56</td>
<td>71</td>
<td>77</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>30B</td>
<td>51</td>
<td>69</td>
<td>75</td>
<td>79</td>
<td>80</td>
<td>81</td>
<td>81</td>
</tr>
<tr>
<td>30C</td>
<td>53</td>
<td>69</td>
<td>75</td>
<td>78</td>
<td>79</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>Average at 30 days</td>
<td>53</td>
<td>70</td>
<td>76</td>
<td>78</td>
<td>79</td>
<td>80</td>
</tr>
<tr>
<td>100A</td>
<td>64</td>
<td>72</td>
<td>78</td>
<td>80</td>
<td>81</td>
<td>82</td>
<td>82</td>
</tr>
<tr>
<td>100B</td>
<td>56</td>
<td>70</td>
<td>76</td>
<td>78</td>
<td>80</td>
<td>81</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>Average at 100 days</td>
<td>60</td>
<td>71</td>
<td>77</td>
<td>79</td>
<td>80</td>
<td>81</td>
</tr>
<tr>
<td>130C</td>
<td>56</td>
<td>70</td>
<td>77</td>
<td>79</td>
<td>79</td>
<td>80</td>
<td>80</td>
</tr>
</tbody>
</table>
Table 2-4: $T_g$ assigned using Tan $\delta$ ($T_{gTD}$)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$T_{gTD}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R1</td>
</tr>
<tr>
<td>7A</td>
<td>59</td>
</tr>
<tr>
<td>7B</td>
<td>60</td>
</tr>
<tr>
<td>7C</td>
<td>57</td>
</tr>
<tr>
<td>Average at 7 days</td>
<td>59</td>
</tr>
<tr>
<td>30A</td>
<td>65</td>
</tr>
<tr>
<td>30B</td>
<td>63</td>
</tr>
<tr>
<td>30C</td>
<td>64</td>
</tr>
<tr>
<td>Average at 30 days</td>
<td>64</td>
</tr>
<tr>
<td>100A</td>
<td>73</td>
</tr>
<tr>
<td>100B</td>
<td>66</td>
</tr>
<tr>
<td>Average at 100 days</td>
<td>69.5</td>
</tr>
<tr>
<td>130C</td>
<td>67</td>
</tr>
</tbody>
</table>

It can be seen that $T_g$ assigned using storage modulus ($T_{gSM}$), loss modulus ($T_{gLAM}$) and Tan $\delta$ ($T_{gTD}$) follow the trend $T_{gSM} < T_{gLAM} < T_{gTD}$. Assignment of $T_g$ using Tan $\delta$ and loss modulus peaks are the more prevalent methods reported in the literature as they are relatively easier to pick and more consistent. Finding $T_g$ from the storage modulus is relatively operator-dependent because of the need to manually fit tangents to the regions below and through the $T_g$ range. ASTM E1640 [13] recommends assigning $T_g$ based on the point of intersection of these tangents, which represents the center of the range of temperatures corresponding to the onset of transition. On the other hand, the loss modulus and Tan $\delta$ peaks generally represent the midpoint temperature of the temperature range over which transition takes place [7], at which point the storage modulus may have lost half or more of its value just below $T_g$. From a structural engineer’s point of view, a temperature which marks the onset of loss in storage modulus may be
the more appropriate upper use temperature, rather than the one at which the storage modulus has been diminished substantially.

Referring to Figure 2-10, an increase in first-run \( T_g \) with age of epoxy was observed. In about 93 days of aging (the number of days between the 7- and 100-days-old specimens) at room temperature, \( T_{gSM} \) increased by 15°C, \( T_{gLM} \) increased by 13°C and \( T_{gTD} \) increased by 11°C. The reason for the increase in \( T_g \) of the ambient temperature cured epoxy aging at ambient temperature will be discussed in Chapter 3. The first-run average \( T_g \) of a 7-day-old specimen based on storage modulus was 40°C. It is precariously low, since a temperature near 40°C is easily attainable on the surface of structure in-service. According to the ACI 440.2R-08 guidelines [12], the anticipated service temperature of an FRP system is recommended to not exceed \((T_g - 15)°C\)". It should be noted that ACI 440.2R-08 defines \( T_g \) based on the loss modulus method, although the guide is silent on the age of the material at the time of testing. The dry \( T_g \) is used for dry conditions, and the wet \( T_g \) is used for wet conditions. For the test method employed in the present investigation, the average dry \( T_{gTD} \) value is 59°C for a 7-day-old specimen. Thus, the service temperature limit for the subject resin system according to ACI is 44°C if the \( T_g \) is to be based on 7-day-old material. The fib Bulletin 14 has a similar guideline for \( T_g \) of resin in relation to the service temperature of the structure. The fib Bulletin 14 recommends assigning \( T_g \) using the DSC technique but has no guidelines with respect to the age of testing or conditioning of specimen prior to testing. According to the guideline, the service temperature should not exceed \((T_g - 20)°C\) and a minimum absolute value of 45°C. Hence owing to the low \( T_g \) value, use of a 7-day-old cured resin could severely limit the upper use temperature of the structure.

The effect of moisture on the \( T_g \) was also evaluated. The average \( T_g \) for three batches of epoxy tested at ages of 30 days (23 days in water) and 100 days (93 days in water) are reported in
Figure 2-11 alongside results for dry (unhydrated) epoxy specimens of similar total age. The $T_g$ assigned for individual specimens using the first DMA scan with respective saturation moisture contents has been tabulated in Table 2-5.

![Figure 2-11: Comparison of $T_g$ for soaked and unhydrated specimens at different ages using storage modulus (SM), loss modulus (LM) and Tan $\delta$ (TD)](image)

Table 2-5: Moisture content and first-run $T_g$ for saturated specimens

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Saturation Moisture Content (% by weight)</th>
<th>$T_{gSM}$ (°C)</th>
<th>$T_{gLM}$ (°C)</th>
<th>$T_{gTD}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30A&lt;sub&gt;h&lt;/sub&gt;</td>
<td>3.0</td>
<td>47</td>
<td>53</td>
<td>78</td>
</tr>
<tr>
<td>30B&lt;sub&gt;h&lt;/sub&gt;</td>
<td>2.4</td>
<td>46</td>
<td>52</td>
<td>77</td>
</tr>
<tr>
<td>30C&lt;sub&gt;h&lt;/sub&gt;</td>
<td>2.8</td>
<td>52</td>
<td>59</td>
<td>85</td>
</tr>
<tr>
<td>Average 30 days</td>
<td>2.7</td>
<td>48</td>
<td>55</td>
<td>80</td>
</tr>
<tr>
<td>100A&lt;sub&gt;h&lt;/sub&gt;</td>
<td>2.5</td>
<td>49</td>
<td>55</td>
<td>81</td>
</tr>
<tr>
<td>100B&lt;sub&gt;h&lt;/sub&gt;</td>
<td>2.6</td>
<td>51</td>
<td>55</td>
<td>82</td>
</tr>
<tr>
<td>100C&lt;sub&gt;h&lt;/sub&gt;</td>
<td>2.4</td>
<td>49</td>
<td>54</td>
<td>80</td>
</tr>
<tr>
<td>Average 100 days</td>
<td>2.5</td>
<td>50</td>
<td>55</td>
<td>81</td>
</tr>
</tbody>
</table>
Referring to Figure 2-11, it can be seen that the $T_g$ of 23-day soaked specimens is comparable to the equivalently aged unhydrated specimens based on storage modulus, whereas it is higher than the unhydrated specimens based on loss modulus and Tan $\delta$. An increase in $T_g$ with moisture content has been reported previously. According to Wu et al. [17], the presence of water (up to 2 weight %) accelerates the curing rate and the evolution of $T_g$ in epoxy resins. Further studies need to be done to check if the increase in $T_g$ is actually due to the progress of a chemical reaction or some other mechanism in the current epoxy resin. For the 93-day soaked specimen, a reduction in $T_g$ was visible based on storage and loss moduli, but the $T_{gTD}$ indicated an increase.

The Tan $\delta$ curve had an obscured peak at around 65°C (Figure 2-12). Yang et al. [18] have also reported the splitting of Tan $\delta$ peaks in aqueous solution. The splitting can be attributed to plasticization of epoxy in water or non-uniform drying during DMA testing, with the obscured peak associated with the $T_g$ of a “wetter” phase and the higher peak being $T_g$ of a “drier” phase. It is also interesting to note that the $T_g$ assigned according to the Tan $\delta$ peak can be deceptive, as the storage modulus of the material decreases considerably at 25°C below the $T_{gTD}$. 
2.3.2 DSC Results

A typical DSC scan (after subtracting the zero line) of a 30-day-old resin sample is shown in Fig. 2-13. The base lines before and after the transition are marked. These extended baselines intersected the line of greatest slope in the transition region at two points. The temperature at the point on the curve corresponding to average of heat flow at these two points was assigned as the glass transition temperature. Figure 2-13 shows a typical DSC scan on a 7-day-old epoxy specimen. The specimen was exposed to two consecutive heat-cool cycles (as discussed in Section 2-2-2). During the first thermal cycle, the specimen undergoes a glass transition at around 40°C. An endothermic peak was also recorded in the thermogram as the specimen undergoes glass transition. This peak is most probably a structural relaxation peak generally associated with epoxy resin aged at a temperature below the $T_g$. As the specimen is heated further (during the first cycle) two exothermic peaks were observed. Exothermic peaks

Figure 2-12: Raw DMA data for a typical specimen soaked for 93 days
indicate chemical reaction of epoxy and amine chemical groups. During the second cycle, no structural relaxation peak was observed as the heating of specimen above $T_g$ during the first cycle erases the effect of physical aging. The increase in $T_g$ (from 41°C to 69°C) due to post curing of resin during heating of specimen can also be seen.

Figure 2-13: Two consecutive DSC scans on a 7-day-old specimen from Batch B’

Figure 2-14 shows a comparison of $T_g$ of three different batches of resin (A’, B’ and C’) tested at ages of 7, 30, and 100 days. The assigned $T_g$ increases with age of the epoxy, as was observed using the DMA technique. The average $T_g$ increased from 40°C to 53°C with the increase in age from 7 days to 100 days. The $T_g$ assigned using DSC was close to the $T_{gSM}$ assigned using DMA. The low value of $T_g$ at the age of 7 days (approximately 40°C) is especially of concern for structural strengthening.
Figure 2-14: Summary of DSC $T_g$ data for epoxy cured for various numbers of days at room temperature, from batches A’, B’, and C’.

2.4 Conclusion

The glass transition temperature of a commercially available ambient temperature cured epoxy resin was characterized using DMA and DSC techniques. The dependence of $T_g$ on method of assignment of $T_g$ was observed. In general, $T_g$ assigned using DSC $\equiv T_{gSM} < T_{gLM} < T_{gTD}$. The increase in $T_g$ with increase in age of epoxy was observed. In about 93 days of aging (between the 7 and 100 days old specimen) at room temperature, $T_{gSM}$ increased by 15°C, $T_{gLM}$ increased by 13°C, $T_{gTD}$ increased by 11°C and $T_g$ assigned using DSC increased by 13°C. Moisture exposure for long duration can affect the glass transition temperature. For the 93-day soaked specimen, a reduction in $T_g$ was visible based on storage and loss moduli, but the $T_{gTD}$ showed an increase. The low value of $T_g$ onset (around 40°C) for a 7-day-old specimen is precariously low considering the fact that such a temperature is easily attainable on the surface of structure in-service.
A limited investigation to enhance the $T_g$ of a generic epoxy resin system was made in the present investigation. For this purpose, a commercially available accelerator for epoxy-amine reactions known as DMP 30 (2,4,6-tris (dimethylaminomethyl) phenol) was used. The formulation ratio for EPON 862 epoxide and isophorone diamine (IPDA) was worked out to be 25.19 grams of IPDA per 100 grams of EPON 862 epoxide. To accelerate the cure and generate an increased temperature due to the exothermic conditions, 1.5% by volume of DMP 30 was added to this generic resin formulation. A significant increase of in DSC $T_g$ for a 7-day-old specimen was observed, as shown in Figure 2-15. But there was a trade-off in the toughness of the resin. The resin specimen molded using the mixture of EPON862/IPDA/ DMP 30 accelerator was actually susceptible to cracking when attempts were made to machine specimens using the as-cast plate.

Figure 2-15: Enhancement in $T_g$ using DMP 30 accelerator with generic resin mixture: (a) EPON 862/IPDA; (b) EPON 862/IPDA/DMP 30.

Although the increase in $T_g$ looked promising, better results may have been obtained if additional time was spent on toughening the system with modifiers. Further exploration of this approach for increasing the $T_g$ of ambient-cured epoxy is left for future work.
Chapter 3

Investigation of Cure Kinetics and Physical Aging Kinetics in Epoxy Resin

3.1 Introduction

The importance of $T_g$ in relation to service temperature has been emphasized in Chapter 2. The $T_g$ can be enhanced by post curing the resin or by physical aging of resin below its $T_g$. Chemical curing improves the cross link density in the network polymers and hence effects the polymer’s properties. Physical aging also affects the physical properties of the resin. The chemical cure kinetics and physical aging kinetics can impact the $T_g$ evolution and creep properties of epoxy resin. Hence, it is important to understand and model the phenomena of chemical cure and physical aging in the resin system under study.

3.1.1 Literature Review on Cure Kinetics of Epoxy Resin

The kinetics of polymerization reactions in epoxy resins has been studied by several authors [19-23]. For this purpose, several techniques such as differential scanning calorimetry (DSC), infrared spectroscopy, dielectric spectroscopy and dielectric thermal analysis have been used. Isothermal and non-isothermal DSC are the most commonly used techniques to model the epoxy cure kinetics. The degree of cure ($\alpha$) of epoxy is the extent of completion of the polymerization reaction. It is expressed in terms of the heat released during the reaction as

$$\alpha = \frac{\Delta H_{reaction}}{\Delta H_{total}}$$

(3-1)
where $\Delta H_{total}$ is the maximum possible heat of reaction of the epoxy-amine reaction and
$\Delta H_{reaction}$ is the actual amount of heat released by the epoxy-amine system. The value of
$\Delta H_{total}$ is dependent on the stoichiometry of the reactants. A stoichiometric ratio of reactants,
such that all the reactants are converted into products will give the maximum value of $\Delta H_{total}$.
Hence a freshly mixed resin has a degree of cure value of 0 and a fully cured resin has a degree of
cure value as high as 1. Cure kinetics are often mathematically expressed in terms of rate of
change of degree of cure with time $(d\alpha/dt)$, also known as the “rate of conversion.” Several
phenomenological models have been developed and used to model cure kinetics. The $n^{th}$ order
reaction model is the simplest model which expresses rate of conversion as in Equation 3-2,

$$\frac{d\alpha}{dt} = K(1 - \alpha)^n$$

(3-2)

where $K$ is a rate constant with an Arrhenius-type dependence on temperature [21]. Epoxy-amine
reactions have also been modeled using the Kamal and Sourour model, which assumes the
reaction to be autocatalytic in nature,

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^n)(1 - \alpha)^n$$

(3-3)

where $k_1$ and $k_2$ are empirically determined rate constants [19][21].

Ruiz et al. [23] describe the “isoconversion map” technique which uses DSC
measurements to graphically predict the degree of cure in thermosetting polymers for varied
thermal histories. This technique overcomes the complication of fitting a multi-parameter kinetics
model to experimentally obtained data since it requires no model fit whatsoever. In the present
investigation, this technique has been adopted to model the cure kinetic behavior for the epoxy
resin system under investigation. Detailed treatment of experimental data to develop iso-conversion maps is discussed in a subsequent section.

3.1.2 Literature Review on Physical Aging Kinetics of Epoxy Resin

The phenomenon of physical aging has been comprehensively reviewed and discussed by several authors [24-26]. The term physical aging was first used by Struik [24] to describe the gradual evolution of glassy polymer towards equilibrium. Struik [24] explains the phenomenon of physical aging based on the concept of free volume and molecular mobility. Molecular mobility is defined as the rate at which the molecular chain configuration changes. Free volume refers to the empty spaces in the molecular arrangement. As the polymer is stored at a temperature below its $T_g$, the free volume starts decreasing towards the equilibrium value as depicted from the plot of specific volume versus temperature (Figure 3-1a). In-turn, the reduction of free volume decreases the mobility of the molecular chain (Figure 3-1b) which decreases the rate of change of free volume with time. This cyclic process goes on until an equilibrium molecular configuration is achieved asymptotically. Physical aging affects several experimentally measurable properties such as specific volume, enthalpy, elastic modulus, creep response, and dielectric properties of the polymer.
Figure 3-1: (a) Specific volume variation with temperature and the deviation of specific volume from equilibrium below $T_g$. (b) Variation of molecular mobility with specific volume

Struik [24] also explained the importance of taking physical aging into consideration in the testing of plastics and studying of long term performance of polymeric materials. Hutchinson [26] has reviewed dilatometry and DSC techniques to characterize physical aging. Dilatometry or volume relaxation measurement, which involves measuring change in length or volume of the polymer, was one of the earliest techniques used to characterize physical aging. Based on dilatometric studies, the non-linearity of isothermal aging with respect to departure from equilibrium has been observed. Another important characteristic of physical aging is its thermoreversibility [24]. Heating a polymeric material to above its $T_g$ brings it in equilibrium (as shown in Figure 3-1) and erases any prior physical aging history of the material. Further storing the material at temperature below $T_g$ initiates the phenomenon of physical aging once again. In this respect physical aging is different from chemical aging which is not thermoreversible.

Differential scanning calorimetry has become a popular technique to characterize and study the phenomenon of physical aging. As the polymer is aged at temperature below $T_g$, the
enthalpy of the polymer starts decreasing towards the equilibrium enthalpy value. Figure 3-2 (reproduced from Hutchinson [26]) shows the specimen being aged at temperature $T_a$ and the decrease in enthalpy from $H_o$ (point A) to $H_t$ (point B) in time $t$. The decrease in enthalpy ($H_t - H_o$) is equal to the difference of area under the endothermic relaxation peak on the DSC curves corresponding to specimen at point A and point B. As the enthalpy of polymer decreases towards the equilibrium value, the area under the endothermic relaxation peak of DSC curve also known as the relaxation enthalpy ($\Delta H$) increases. Relaxation enthalpy has been used to study physical aging kinetics of epoxy resin [28-30]. Plazek and Frund [30] showed the variation of relaxation enthalpy with increase in aging time for a fully cured Epon 828/MDA epoxy resin samples physically aged at 130°C (Figure 3-3). The paper also discusses the linearity of endothermic peak areas with the logarithm of aging time. The temperatures corresponding to the peak of relaxation enthalpy and onset of glass transition temperature have also been reported to evolve linearly with the logarithm of aging time [29][30]. Hence, the onset of $T_g$ can also be used as a measure of physical aging.
Figure 3-2: Evolution of enthalpy towards equilibrium (Stage A: Un-aged specimen, Stage B: Partially aged specimen) and heat capacity curves at the two stages of aging [26].
To explain the kinetics of physical aging, Tool [27] conducted dilatometric experiments on inorganic glasses. The concept of fictive temperature ($T_f$) was introduced to explain the dependence of aging kinetics on aging temperature, $T_a$, and the instantaneous state or structure of the glass. Fictive temperature is defined as the temperature at which the aging material has the same structure as the material in equilibrium if it was instantaneously cooled to equilibrium. It is an artificial temperature which is equal to the glass transition temperature when aging time is zero and equal to aging temperature at infinite aging time. Figure 3-4 (reproduced from [27]) shows how $T_f$ is assigned for an aging material where $l_0$ is the initial length, $l_i$ is the length after aging time $t$, and $l_\infty$ is the equilibrium length at aging temperature $T_a$. 

Figure 3-3: Endothermic DSC peaks for fully cured Epon 828/MDA samples physically aged at 130°C for aging times up to 648 hours (reproduced from [22])
Figure 3-4: Graphical assignment of fictive temperature ($T_f$) (reproduced from [26])

Structural relaxation kinetics is studied by variation of physically measurable quantities such as enthalpy, specific volume or length from initial value to the equilibrium value. The process of structural relaxation is characterized by a single relaxation time $\tau$ or a distribution of relaxation times. Tool’s concept of fictive temperature was further developed by Moynihan et al. [31] to give an expression for structural relaxation time which is known as the Tool, Narayanaswamy, and Moynihan model or the TNM model. The TNM model expresses relaxation time as a function of aging temperature, $T_a$, and fictive temperature, $T_f$, according to Equation (3-4)

$$
\tau(T, T_f) = \tau_0 \exp\left[\frac{x \Delta h^*}{RT} + \frac{(1-x) \Delta h^*}{RT_f}\right]
$$

(3-4)

The parameter $x$ defines the relative contribution of temperature and structure on the relaxation time. Parameter $\tau_0$ is the relaxation time in equilibrium at infinitely high temperature, and $\Delta h^*$ is the apparent activation energy. The deviation of the measured property from its value at
equilibrium is denoted by \( \delta \). For example, if the measured property is enthalpy \( (H) \), \( \delta \) is given according to Equation (3-5)

\[
\delta = \frac{(H_t - H_\infty)}{H_\infty}
\]  

(3-5)

where \( H_\infty \) is the equilibrium value of enthalpy. The relation between the deviation from equilibrium, \( \delta(t) \), and relaxation time, \( \tau \), is given according to a stretched exponential function also known as Kohlrausch-Williams-Watts function, where \( \delta_0 \) is the initial value of \( \delta(t) \)

\[
\delta(t) = \delta_0 \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right]
\]  

(3-6)

The TNM parameters \((x, \beta, \Delta h^*, \tau_0)\) are dependent on material being studied and are obtained by an appropriate analysis of the experimental data.

3.2 Experimental Program

The experiments for studying kinetics of chemical cure and physical aging were done using differential scanning calorimetry on MB2ace Saturant\textsuperscript{R} (BASF Corporation) epoxy resin. The experimental procedures are discussed in the following sections.

3.2.1 Chemical Cure Kinetics

The investigation on cure kinetics was done by using differential scanning calorimetry to study the progress of chemical cure by heating freshly mixed epoxy resin at different heating rates. The enthalpy of reaction between epoxide and amine group was measured using DSC scans done at different heating rates. By studying the progress of the chemical reaction at different
heating rates, a model to predict the degree of cure ($\alpha$) after a given thermal exposure can be developed. In the present study, Perkin Elmer’s DSC 8500—a power compensated DSC—was used. Large volume stainless steel pans (Perkin Elmer) of 60 $\mu$L capacity with a lid and rubber seal capable of sustaining high internal pressure was used in the scans. Thermal scans were done at 3°C/min, 5°C/min, 8°C/min and 10°C/min from 0°C to 200°C. Specimen mass of around 5 mg was used in every scan.

3.2.2 Physical Aging Kinetics

To study physical aging kinetics, differential scanning calorimetry was utilized. The DSC scans were done at 3°C/min from 0°C to 80°C as the interest was in studying the phenomena of glass transition and endothermic relaxation peak near $T_g$ to characterize physical aging. A separate investigation to check the thermoreversibility of physical aging was done which has been included in Appendix D.

3.3 Results and Discussion

This section presents the results of the investigation on chemical cure kinetics and physical aging kinetics for the epoxy resin under study.

3.3.1 Model for Prediction of Degree of Cure ($\alpha$)

The results for the DSC scan on freshly mixed epoxy at different scanning rates of 3°C/min, 5°C/min, 8°C/min and 10°C/min are shown in Figure 3-5. The DSC scans have their baselines tilted as baselines were not subtracted in the data shown. Figure 3-5 shows a double
peaked cure exotherm for the epoxide-amine reaction. A B-spline function was fitted as the baseline [14]. The area integral was calculated using Origin Pro 8® to evaluate the heat of reaction at different heating rates. The reaction enthalpy value was around 300 J/g in each case. The consistency in reaction enthalpy indicates that the epoxy-amine reaction was close to completion at each dynamic scan rate.

Figure 3-5: DSC scans and heat of reaction value of freshly mixed resin at (a) 3°C/min (b) 5°C/min (c) 8°C/min and (d) 10°C/min.

DSC scans at different heating rates were used to calculate degree of cure (α) versus time using eq. (3-7)
\[ \alpha(t) = \frac{A_t}{A_{total}} \]  

(3-7)

where \( A_{total} \) corresponds to the total area under DSC curve and \( A_t \) is the partial area under DSC curve up to time \( t \). Figure 3-6 shows the degree of cure versus time plot for different heating rates.

Figure 3-6: Degree of cure versus time at different heating rates

The isoconversion modeling technique as reported by Ruiz et al. [23] was followed to develop the prediction model for degree of cure. The method is called “iso-conversion technique” because it evaluates the point with same degree of cure on DSC curves but at different time and temperatures and then uses it to predict the time-dependent variation of degree of cure at different heating rates or at different isothermal conditions. The time-heating rate function for constant degree of cure \((\alpha)\) can be expressed as
where $t$ is time, $\phi$ is the heating rate in °C/min, and $P$ and $Q$ are two constants dependent on degree of cure, $\alpha$. From the degree of cure versus time plot (Figure 3-6), curing time values corresponding to constant degrees of cure for different heating rates were picked. For example, Figure 3-6 shows the method for picking curing time values at different heating rates for degree of cure value of 0.4. In a similar manner points corresponding to degree of cure values from 0.02 to 0.95 were picked and plotted as shown in Figure 3-7. Equation (3-9), which is obtained by rearranging Equation 3-8 was used to fit the experimentally obtained discrete points (also shown in Figure 3-7).

$$t = 10^P (\phi^Q)$$  \hspace{1cm} (3-9)
The dependence of parameters $P$ and $Q$, which were obtained by fitting the Equation 3-9, on degree of cure ($\alpha$) was studied. Figure 3-8 shows the dependence of fit parameter $P$ and $Q$ on degree of cure. Equations of the form (3-10a) and (3-10b) provided good fits to the data.

\[
P = 0.08915 + \alpha^{0.1984} + e^{(0.01236(\alpha-1.932))}
\]

(3-10a)

\[
Q = -0.8729e^{(0.043\alpha)} + 0.235e^{(-27.78\alpha)}
\]

(3-10b)

Since the thermal scans were done at a constant temperature ramp rate, the temperature ($T$) and heating rate ($\phi$) can be related according to Equation 3-11.

\[
T = \phi t + T_i
\]

(3-11)

where $T_i$ is the initial temperature, which in the current case is 0°C. Also, using Equation 3-9 to eliminate $\phi$ from Equation 3-11, cure temperature $T$ (°C) can be expressed in terms of curing time $t$ (minutes).

\[
T = \left(\frac{t^{1+Q}}{Q}\right)/(10^P/Q)
\]

(3-12)
Equations (3-9) and (3-10) can be used to generate a series of curves corresponding to values of degree of cure relating heating rate and time. Similarly, Equations 3-12 and 3-10 can be used to generate a series of curves corresponding to values of degree of cure relating cure time and cure temperature. These two set of curves together constitute the isoconversion map which can be used to predict the degree of cure of epoxy for a given sequential combination of heat ramp and isothermal cure condition. The isoconversion map developed using the technique discussed above is shown in Figure 3-9. For a given duration of time, the degree of cure can be predicted for a certain temperature ramp rate using the isoconversion curves shown in red. Likewise, for a given time, the degree of cure can be predicted for a selected isothermal temperature using the isoconversion curves shown in black.

Figure 3-9: Isoconversion map for MBrace saturant resin
To draw conclusions regarding the progress of chemical cure of MBrace saturant resin cured and aged at ambient temperature, a 7-day-old sample was studied using the DSC technique. As seen in Figure 3-11, the residual enthalpy of reaction was calculated to be 64 J/g. Hence, the degree of cure of the sample calculated using Equation 3-7 is \((300-64)/300\) or 0.78.

![Figure 3-10: Residual enthalpy of a 7-day-old epoxy sample cured at 22°C temperature.](image)

From the isoconversion map shown in Figure 3-9 it can be seen that practically no change in degree of cure of a material with degree of cure of 0.78 can take place by aging it isothermally below a temperature of around 70°C. So it can be concluded that, for a 7-day-old epoxy resin, cured and stored at 22°C, no progress in chemical cure takes place at around room temperature. Hence the experimentally observed increase in \(T_s\) with the age of this ambient temperature cured resin cannot be attributed to progress in chemical cure. The usefulness of the isoconversion map can be in developing a post-curing thermal scheme to advance the degree of cure. Consider a case where the degree of cure of resin is to be enhanced from 0.8 to 0.9 by maintaining it isothermally at a temperature for some duration of time. Using Figure 3-9, if this resin sample is subjected to a temperature of 80°C for 2000 minutes (1.38 days), as shown by blue colored horizontal line on Figure 3-9, degree of cure can be enhanced from 0.8 to 0.9.
3.3.2 Physical Aging Evolution Model

An investigation of physical aging was done on MBrace saturant resin cast and aged at 22°C for 10 days and then subjected to 40°C for variable amounts of time. As can be seen from Figure 3-11, the $T_g$ monotonically increases from an initial value of 44°C to a maximum value of 64°C with aging times of up to 240 hours at 40°C. Meanwhile, the residual heat of enthalpy ranges between 66 and 72 J/g over the same exposure period. The non-monotonic variation in heat of enthalpy is believed to be due to material variability or uncertainty in fitting the baseline to the DSC data. It is therefore concluded that exposure to 40°C did not advance the chemical cure. It can also be concluded by logical extension that no progress in chemical cure takes place for a 10 days old epoxy resin if stored at 22°C. This fact is also supported by isoconversion map predictions.

Figure 3-11: Effect of 40°C exposure on $T_g$ and residual cure enthalpy for resin aged for 10 days at room temperature.
Since Figure 3-11 supports the argument that the increase in $T_g$ is due to physical aging and not advancement of cure, a measure of physical aging was sought. Typically, variation in relaxation enthalpy is used to characterize the extent of physical aging. The increase in enthalpy relaxation, due to physical aging, for one particular batch of resin (Batch A’) cured and aged at 22°C is shown in Figure 3-12. However, inconsistent trends in enthalpy relaxation and high batch-to-batch scatter led to the use of $T_g$ as the physical aging parameter rather than enthalpy relaxation.

![Figure 3-12: Evolution of relaxation enthalpy for resin cured and aged at 22°C for 7, 30, and 100 days](image)

The evolution of $T_g$ according to DSC tests at three different aging temperatures is summarized in Figure 3-13. The experimental data for the $T_g$ evolution at 22°C were the average of three different batches tested at the ages of 7, 30, and 100 days as discussed in Section 2.2.2. In Figure 3-13, aging time of 0 days corresponds to 7 days of aging at 22°C and the age refers to the
time of exposure to the aging temperature beyond the first 7 days of curing at 22°C. For the purpose of comparison, all experimental data points were slightly shifted vertically (±2°C) so that the $T_g$ value at the common starting point (age of 0 days) was equal to the average of experimental data at that age. Curve fitting was utilized to fit the experimental data at the three different aging temperatures. The fit functions were used to develop an “extent of aging” parameter, as explained later. The rate of $T_g$ change in the first week was very low at 22°C in comparison to that at 30°C and 35°C. At temperatures of 30°C and 35°C, the evolution of $T_g$ slowed down markedly after first 14 days of aging as the epoxy reached closer to equilibrium at the aging temperature, hence slowing down the structural relaxation process considerably.

![Figure 3-13: $T_g$ evolution with aging at different temperatures](image)

Figure 3-13: $T_g$ evolution with aging at different temperatures

An “extent of aging” parameter ($\beta$), according to eq. (3-13), was defined as the ratio of $T_g$ at the instantaneous time at temperature $T$ to the $T_g$ at infinite aging time at temperature $T$. 
\[ \beta = \frac{T_g(\text{in } K)}{T_{g0}(\text{in } K)} \]  
(3-13)

The “extent of aging” value of 1 means that the aging polymer has reached its equilibrium at the particular temperature. Smaller fractional values of \( \beta \) of an aging polymer imply that the polymer is farther away from equilibrium. The mathematical functions for evolution of \( \beta \) depending on the aging temperature \( T \) are expressed by Equations 3-14a, b and c.

\[ \beta_{22^\circ C} = \frac{40.46 + 11.54(t^2)}{20.26 + t^2} \frac{40.76 + t^2}{52 + 273} \]  
(3-14a)

\[ \beta_{30^\circ C} = \frac{55.58e^{(2.963)(10)^{-5}t} - 15.56e^{-0.2421t} + 273}{56 + 273} \]  
(3-14b)

\[ \beta_{35^\circ C} = \frac{59.9e^{(8.816)(10)^{-6}t} - 19.77e^{-0.4689t} + 273}{60 + 273} \]  
(3-14c)

From these functions, it can be seen that the projected \( T_g \) at infinite time at aging temperatures of 22°C, 30°C, and 35°C are 52°C, 56°C, and 60°C, respectively.

### 3.4 Conclusion

The cure kinetics of the epoxy resin was studied using DSC scans on freshly mixed resin at different heating rates. The “isoconversion map” technique was followed to develop a map to predict degree of cure (\( \alpha \)) for a given temperature profile. The isoconversion map was used to conclude that no progress in chemical cure occurs in epoxy resin cured and aged at 22°C beyond the first 7 days of curing. For a 7-day-old resin a minimum temperature of 70°C is required to initiate the chemical reaction and to advance the degree of cure. The map is useful in developing a thermal program to post cure the epoxy resin to desired value of degree of cure.
DSC scans on a 10-day-old resin sample, cured at 22°C and aged at 40°C beyond the first 10 days, showed an evolution of $T_g$ without any change in residual reaction enthalpy, which provides evidence of physical aging. To study the kinetics of physical aging, specimens were aged at 22°C, 30°C, and 35°C beyond the first 7 days of cure at 22°C. The $T_g$ evolution at different temperatures was measured using DSC. An “extent of aging” parameter ($\beta$) was defined to parameterize the evolution of epoxy resin towards equilibrium at the aging temperature.
Chapter 4

Prediction of Tensile Creep Behavior in Epoxy Resin

4.1 Introduction

Externally bonded FRP materials are being increasingly used repair and strengthening of concrete, masonry, steel and timber structures in civil infrastructure. The system relies on a polymer material—typically epoxy resin—to transfer load from the superstructure to the fibers. Under sustained loading the epoxy adhesive layer and the FRP laminate can exhibit time dependent deformation. Among these two components, the epoxy layer is most susceptible to creep deformation. Hence, it is imperative to primarily understand and predict creep in epoxy resin itself to make long term behavior predictions of FRP strengthening systems.

As explained in Chapter 1, the externally bonded FRP system is generally hand laid up on the structure. The system is cured at ambient temperature. The ambient temperature cured epoxy resin, in general, is not 100% chemically cured. In practice, epoxy resin manufacturers blend the resin system with accelerant to increase the rate of chemical cure reaction. The partially cured epoxy resin exhibits magnified creep at temperature close to $T_g$. As emphasized in Chapter 2, the $T_g$ of ambient temperature cured resin can be close to the service temperature of the structure and creep of the epoxy can therefore influence the long term performance of the structure under load.

Glassy polymers such as ambient cured epoxy resin tend to evolve from a non-equilibrium state towards equilibrium resulting in changes in physical properties. This phenomenon is called physical aging. It is also known as structural relaxation, annealing or stabilization. As the material undergoes physical aging, it becomes more glass-like in terms of its
mechanical properties. Aging results in an increased stiffness, brittleness and decreased creep rate of the material. Hence creep in an ambient temperature cured epoxy resin is dependent upon the extent of physical aging of the resin.

4.2 Objectives

The objective of this portion of the investigation is to characterize the creep behavior in plain epoxy as a function of aging time ($t_a$) and test temperature ($T$). Furthermore, an experimentally measurable quantity to characterize the extent of aging at various aging times and temperatures, as developed in Section 3.3.2, is utilized to relate effect of physical aging on experimentally observed creep in epoxy resin. Finally, a model to predict creep in the evolving epoxy resin based on the aging parameter is developed.

4.3 Literature Review

Polymeric materials such as epoxy resin are viscoelastic in nature and exhibit time dependent deformation. A typical creep response in a viscoelastic material has been depicted in Figure 4-1 [32, 33]. In the early stage of creep test, the strain rate is high and slowly decreases as the test progresses. This initial part of creep curve is known as primary creep region. Beyond a certain time into the test, the creep rate becomes steady. This region of the creep curve is known as secondary creep. Depending upon the stress level and ductility of the material, a tertiary region in the creep curve is observed where strain rate increases with time before eventual creep rupture of the material.
Figure 4-1: Typical creep response of viscoelastic material

Mathematical models to depict the creep behavior have been extensively reported in the literature [32]. The simplest and the easiest to visualize are the spring and dashpot models. Some of the common spring dashpot models along with the mathematical representation are provided in Table 4-1. Maxwell’s model is the simplest and represents creep in a very crude sense. It works well for modeling secondary creep when the strain rate is steady. The Kelvin-Voigt model has an asymptotic time response which is closer to experimentally observed creep characteristics but it cannot model the instantaneous elastic response to a given stress. Burger’s model works well in this regard. It has been used by Majda et al. [34] to model the creep response of ambient temperature cured epoxy resin. The instantaneous elastic response and gradual decrease in strain rate of the material under sustained loading is captured well by Burger’s model. Characterizing the four elements of Burger’s model is complicated in comparison to the two element Maxwell and Kelvin-Voigt models but less complicated than Maxwell-Wiechert model.
Table 4-1: Phenomenological models for modeling creep behavior

<table>
<thead>
<tr>
<th>Viscoelastic Model</th>
<th>Mathematical Relation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Maxwell Model:</strong></td>
<td>For step stress response</td>
</tr>
</tbody>
</table>
|                           | \[
|                           | \[ \frac{\varepsilon_t}{\sigma} = \frac{t}{E} + \frac{1}{\eta} \] |
| **Kelvin-Voigt Model**    | For step stress response |
|                           | \[
|                           | \[ \frac{\varepsilon_t}{\sigma} = \frac{1}{E} (1 - e^{-\frac{Et}{\eta}}) \] |
| **Burger’s Model**        | For step stress response |
|                           | \[
|                           | \[ \frac{\varepsilon_t}{\sigma} = \frac{1}{E_1} + \frac{t}{\eta_1} + \frac{1}{E_2} (1 - e^{-\frac{E_2 t}{\eta_2}}) \] |
| **Maxwell–Wiechert Model**| Governing differential equation |
|                           | \[
|                           | \[ \sigma = \sum \sigma_j \]
|                           | \[
|                           | \[ \frac{d\varepsilon_t}{dt} = \frac{\sigma_j}{\tau_j} + \frac{1}{K_j} \int \frac{d \sigma_i}{dt} dt \] \]

Findley’s power law model for modeling creep has been used in many studies [35-36].

For a single step stress loading, it is mathematically represented as
\[
\varepsilon_t = \varepsilon_0 + \sigma^k A t^b
\]  
(4-1)

Where \(\varepsilon_t\) is instantaneous strain, \(\varepsilon_0\) is the initial elastic strain, \(\sigma\) is the applied stress, \(t\) is the creep duration and \(A, b\) and \(k\) are empirically determined constants. Typically, \(k=1\) for polymers. Therefore Equation 4-1 can be divided by stress, \(\sigma\), so that both sides of the equality are in units of compliance [32]. The phenomenon of creep is also dependent on the test temperature, \(T\). The effect of temperature can be incorporated in the power law by assuming creep activation energy, \(Q\). The creep law is modified as shown in Equation 4-2.

\[
\varepsilon_t = \varepsilon_0 + \sigma^k A t^b e^{-Q/RT}
\]  
(4-2)

In the present investigation a modified form of the Findley creep power law (Equation 4-2) is used to model the creep deformation of epoxy resin.

The time-temperature superposition principle is used to account for the effect of temperature on the creep of polymeric materials. Temperature affects the chain mobility and deformation in polymers. At higher temperatures, molecular mobility is high and hence the creep compliance is also high [41]. According to the time temperature superposition principle, momentary creep compliance, \(D = \varepsilon/\sigma\), at two different temperatures, \(T_1\) and \(T_2\), are related as

\[
D(t, T_2) = D(a_{T_2} t, T_1).
\]  
(4-3)

The parameter \(a_{T_2}\) is called the temperature shift factor. The time-temperature superposition principle enables the accelerated creep testing of polymeric materials. Short duration creep compliance values are measured at two or three different temperatures and then shifted on the time scale to construct the master creep compliance curve at the selected reference temperature. The procedure is illustrated in Figure 4-2, where the creep response at temperature \(T_1\) and \(T_2\) are used to create a master creep curve for creep compliance at temperature \(T_1\).
Barbero et al. [37] report that the time-temperature superposition principle does not work for modeling a material undergoing physical aging during a creep test. Time-temperature superposition, as traditionally used, works only for modeling a material being crept at a temperature well below $T_g$, where relaxation time scale is much greater than the test duration.

The time-aging time superposition principal was developed to address the previously mentioned shortcomings of the time-temperature superposition by Struik [24]. A master creep curve for polymeric material of particular age can be generated by horizontally shifting momentary creep curves of the material at different ages. The time aging time superposition can be mathematically expressed as

$$D(t_o) = D(a_t e^{r_{ref}})$$  \hspace{1cm} (4-4)
where \( t_e \) is the aging time, \( D(t_e) \) is the compliance at aging time \( t_e \), \( t_{\text{ref}} \) is the reference age relative to which other creep curves are shifted, and \( a_{t_e} \) is the aging time shift factor. The creep compliance curves are horizontally shifted by a magnitude of \( \log(a_{t_e}) \) towards the reference curve on the creep compliance and log (time) plot to generate the master curve. The logarithm of \( a_{t_e} \) varies linearly with aging time and the slope of the curve is known as the shift rate, \( \mu \). The shift rate is indicative of the aging intensity of the specimen and is mathematically expressed using Equation (4-5)

\[
\mu = \frac{d\left(\log(a_{t_e})\right)}{d\left(\log(t_e)\right)} \tag{4-5}
\]

Struik [24] suggested the use of momentary creep responses of a polymer at different aging times to construct the master curve. The momentary creep curves include the creep response of the material with no effect of aging included in it. In general, the creep response for time duration one tenth of the age of material is considered untainted by the effect of aging. Figure 4-3 shows multiple short duration creep tests done on polyvinyl chloride. The specimens were quenched from a temperature above \( T_g \) to erase the aging history and then stored at 40°C for time up to four years. The creep curves at different ages (0.03 days to 1000 days) were shifted to close coincidence with the 1000-day-aged material to produce the master creep curve for material aged for 1000 days. In this manner, the creep behavior of 1000-day-old material is characterized to test times longer than any one individual test on similar-aged material.
Beckman et al. [38] utilized the time-aging time superposition to investigate the creep behavior of syndiotactic polystyrene. The aging shift factor, $\alpha_t$, was utilized to study the aging kinetics in the material. The study also reports the usage of only vertical shifts of momentary creep curves to construct a master curve at temperatures above $T_g$.

The creep response prediction for a material being aged isothermally can be modeled using time-aging time superposition discussed above. However, only few models exist on predicting creep response of material undergoing physical aging under non-isothermal conditions. Bradshaw and Brinson [39] studied the creep response of carbon fiber laminates with polyimide resin matrix after a temperature up-jump and down-jump during aging. The material under study was aged at temperature $T_0$ and then after some time temperature was step increased or decreased to $T_1$ and material was tested at various times after the temperature jump to $T_1$. Figure 4-4
schematically shows the non-isothermal aging of specimen and the stress strain history of the material under study. The concept of effective aging time for which aging time superposition is applicable was introduced. Effective aging time takes the non-linearity of aging at different temperatures into account and has been used to derive the aging shift factor, \( a_{t_e} \), and temperature shift factor, \( a_T \), for temperature up-jumps and down jumps.

Guo et al. [40] describe experimental creep behavior after nonisothermal aging. A model known as the Kovacs-Aklonis-Hutchinson-Ramos (KAHR) model was utilized to study the relationship between thermodynamic properties and creep response observed experimentally and to predict the creep response of polymer after temperature up-jump or down-jump.

In the present investigation, an attempt has been made to develop a model which utilizes glass transition temperature \( (T_g) \) measurement to develop an “extent of aging” parameter which is

Figure 4-4: Schematic showing temperature up-jump before creep testing of specimen to simulate nonisothermal aging (reproduced from [39])

Guo et al. [40] describe experimental creep behavior after nonisothermal aging. A model known as the Kovacs-Aklonis-Hutchinson-Ramos (KAHR) model was utilized to study the relationship between thermodynamic properties and creep response observed experimentally and to predict the creep response of polymer after temperature up-jump or down-jump.

In the present investigation, an attempt has been made to develop a model which utilizes glass transition temperature \( (T_g) \) measurement to develop an “extent of aging” parameter which is
linked to the creep response of the polymer. The novelty of this technique is in the ease with which aging can be characterized for a complex thermal history of the polymer, which governs its creep behavior. The advantage of using this technique over preceding work to model non-isothermal aging is that creep response is not derived from parameters of a structural recovery model but a more tangible experimentally measured quantity.

4.4 Experiment

4.4.1 Tensile Creep Test Specimen Preparation

To study the creep behavior of plain epoxy resin, tensile coupons of plane resin of approximately 152.4 mm (6 inch) length, 12.7 mm (0.5 inch) width and 6.35 mm (0.25 inch) thickness were tested under constant loading. The specimen was made by first molding 6.35 mm (0.25 inch) thick resin sheet and then cutting it to suitable dimensions. For making the resin sheet, MBrace® saturant resin (BASF Corporation) was mixed according to the manufacturer’s recommendation. The resin was degassed in a vacuum chamber and then poured into a mold (Figure 4-5). The mold was assembled over a polytetrafluoroethylene (PTFE) block. An aluminum frame was placed on the PTFE block with caulking all around the periphery. Two 6.35 mm (0.25 inch) steel rods of equal length were placed at appropriate distance inside the frame to control the thickness of the cast sheet. A top PTFE plate rested over the steel rods to make a closed mold assembly. The frame and steel rods were sprayed with release agent before pouring the mixed, degassed resin.
The sheet was de-molded after minimum 5 days of curing at room temperature. It was then cut into 0.5 inch wide and 6 inches long specimen using a diamond saw. Water spray was used in the cutting process to clean the blade and to prevent the generation of resin dust. The specimen was quickly wiped after cutting to minimize moisture absorption. The cut specimens were then stored and aged in a desiccator with anhydrous calcium sulfate based desiccant.

4.4.2 Creep Test Set-up

Creep tests on the resin coupons were carried out using lever-arm test frames manufactured by the Applied Test Systems Inc. (Butler, Pennsylvania). The test frames have an adjustable lever arm ratio which can be changed according to load requirement (Figure 4-6). In the present study, a lever arm ratio of 3:1 was used for all the creep tests. The frames are equipped with a furnace for running creep tests at desired temperatures with a very tight control (±1°C) over test temperature. A built-in fan helps to circulate air and reduce temperature gradient.
in the furnace. An external temperature controller is used to control the temperature of the creep oven. The room temperature creep tests were done with the furnace open in a room with good control over temperature fluctuations (22±2°C). A temperature logger was used to record the test temperature during the creep tests. Weight plates are loaded on a motorized movable platform which is used for slow and smooth loading and unloading of the specimen. A position sensor attached on the lever arm triggers the vertical movement of the load train to ensure that the lever arm remains horizontal even after considerable deformation of the specimen.

Figure 4-6: Lever arm creep frame

To minimize bending due to machine misalignment, double knife edge alignment couplings were used in the load train. Two different types of grip were used on the two creep
frames. One was a modified wedge grip assembly and the other was a custom-made clamp grip assembly (shown in Figure 4-7). Figure 4-7 also shows the extensometers mounted on opposite faces of the specimen to measure average tensile strain and also to evaluate the bending in the specimen. Strain gage based extensometers were preferred over strain gages mounted directly to the specimen because polymeric resins used to attach strain gages at ambient temperature are also susceptible to creep. The strain gages inside the extensometers are bonded using high-temperature resins and were rated for use in temperatures exceeding the highest test temperature in the current investigation. The extensometers used were all 0.5 inch in gage length and were manufactured by MTS Systems Corp. (Model no. 632.31E-24) and Epsilon Technology Corp. (Model no. 3442).

During the initial setup of the load frames the machine alignment was verified by testing and evaluating the expected strain and elastic modulus of a rectangular cross-section aluminum coupon. During the test, specimen was loaded and the oven heat was turned on at the same time. Elevated temperature could not be equilibrated prior to the application of load because too much deformation was induced on the specimen by the grips and extensometers.

Average creep compliance \( (D) \) is calculated as shown in Equation 4-1, where \( \varepsilon_A \) and \( \varepsilon_B \) are the total strains measured by the two extensometers on the opposite faces of specimen and \( \varepsilon_{A0} \) and \( \varepsilon_{B0} \) are the instantaneous elastic strains measured by two extensometers.

\[
D = \frac{\varepsilon_A + \varepsilon_B}{2\sigma} - \frac{\varepsilon_{A0} + \varepsilon_{B0}}{2\sigma} \quad (4-1)
\]

Instantaneous elastic strain \( (\varepsilon_{A0} \text{ and } \varepsilon_{B0}) \) in the case of test done at 22°C was the strain corresponding to the instant the specimen was loaded. For tests done at 30°C and 35°C, the strain at the instant of 10 minutes into the test (after equilibrium temperature was reached) was assigned as the instantaneous elastic strain.
4.3.3 Creep Test Program

The creep test program was designed to study the effect of temperature and aging on the creep response of plain epoxy resin. Epoxy coupons were tested at three different ages of 7, 30 and 100 days and temperatures of 22°C, 30°C and 35°C. The specimens were all aged at room temperature—approximately 22°C. The rationale for choosing the test temperatures was to evaluate the creep behavior at different temperatures below the $T_g$ which are practically achievable for structures in service. Creep tests were carried out for a duration of approximately 5000 minutes. Table 4-2 summarizes the creep test matrix.
Table 4-2: Number of specimens tested for each combination of age (prior to test) and temperature during test

<table>
<thead>
<tr>
<th></th>
<th>Temperature-22°C</th>
<th>Temperature-30°C</th>
<th>Temperature-35°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Age-7 Days</td>
<td>3</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Age-30 Days</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Age-100 Days</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

According to the test matrix, a minimum of three specimens were tested for 9 different testing conditions. Specimens were named as XXD-YY°C-Z where XX represents the age in days, YY represents the test temperature in °C and Z represents the batch name. For example, 30D-35°C-1 represents a 30 days aged specimen tested at 35°C belonging to Batch 1. The specimens tested at 22°C were tested at a stress level close to 10 MPa whereas the specimens at 30°C and 35°C were tested at stress level close to 2 MPa (except one, 100D-35°C-17, which was tested at 10.29 MPa). The linearity of creep response with stress at higher creep temperatures was checked by testing one particular specimen at stress level of 10.29 MPa.

Specimen 7D-22°C-2 was crept for shorter duration of time (approximately 1000 minutes). The results of this test, along with momentary creep results for specimens from the same batch of resin at the age of 3 and 5 days, were used to study the validity of time-aging time superposition principle and create a master curve for 7D-22°C-2 creep response. The details of this investigation has been included in Appendix B. Table 4-3 summarizes the individual specimen dimensions and stress levels for the creep test.
Table 4-3: Summary of creep specimen dimensions and test stress levels

<table>
<thead>
<tr>
<th>Specimen Name</th>
<th>Width (mm)</th>
<th>Thickness (mm)</th>
<th>Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7D-22°C-1</td>
<td>0.515</td>
<td>0.230</td>
<td>8.73</td>
</tr>
<tr>
<td>7D-22°C-2</td>
<td>0.495</td>
<td>0.265</td>
<td>7.88</td>
</tr>
<tr>
<td>7D-22°C-3</td>
<td>0.476</td>
<td>0.232</td>
<td>9.37</td>
</tr>
<tr>
<td>30D-22°C-4</td>
<td>0.450</td>
<td>0.230</td>
<td>10.00</td>
</tr>
<tr>
<td>30D-22°C-5</td>
<td>0.466</td>
<td>0.251</td>
<td>8.84</td>
</tr>
<tr>
<td>30D-22°C-6</td>
<td>0.463</td>
<td>0.210</td>
<td>10.64</td>
</tr>
<tr>
<td>100D-22°C-7</td>
<td>0.462</td>
<td>0.234</td>
<td>9.57</td>
</tr>
<tr>
<td>100D-22°C-8</td>
<td>0.460</td>
<td>0.244</td>
<td>9.22</td>
</tr>
<tr>
<td>100D-22°C-9</td>
<td>0.484</td>
<td>0.240</td>
<td>10.69</td>
</tr>
<tr>
<td>7D-30°C-10</td>
<td>0.522</td>
<td>0.234</td>
<td>1.69</td>
</tr>
<tr>
<td>7D-30°C-11</td>
<td>0.513</td>
<td>0.223</td>
<td>1.81</td>
</tr>
<tr>
<td>7D-30°C-12</td>
<td>0.550</td>
<td>0.229</td>
<td>1.97</td>
</tr>
<tr>
<td>7D-30°C-13</td>
<td>0.520</td>
<td>0.250</td>
<td>1.59</td>
</tr>
<tr>
<td>7D-30°C-14</td>
<td>0.460</td>
<td>0.254</td>
<td>1.77</td>
</tr>
<tr>
<td>30D-30°C-10</td>
<td>0.522</td>
<td>0.234</td>
<td>1.69</td>
</tr>
<tr>
<td>30D-30°C-12</td>
<td>0.524</td>
<td>0.236</td>
<td>1.67</td>
</tr>
<tr>
<td>30D-30°C-13</td>
<td>0.510</td>
<td>0.245</td>
<td>1.65</td>
</tr>
<tr>
<td>100D-30°C-10</td>
<td>0.466</td>
<td>0.220</td>
<td>2.02</td>
</tr>
<tr>
<td>100D-30°C-12</td>
<td>0.492</td>
<td>0.245</td>
<td>1.72</td>
</tr>
<tr>
<td>100D-30°C-13</td>
<td>0.520</td>
<td>0.246</td>
<td>1.62</td>
</tr>
<tr>
<td>7D-35°C-15</td>
<td>0.448</td>
<td>0.240</td>
<td>0.87</td>
</tr>
<tr>
<td>7D-35°C-16</td>
<td>0.466</td>
<td>0.232</td>
<td>0.86</td>
</tr>
<tr>
<td>7D-35°C-17</td>
<td>0.447</td>
<td>0.256</td>
<td>0.81</td>
</tr>
<tr>
<td>30D-35°C-15</td>
<td>0.460</td>
<td>0.249</td>
<td>0.81</td>
</tr>
<tr>
<td>30D-35°C-16</td>
<td>0.480</td>
<td>0.238</td>
<td>0.81</td>
</tr>
<tr>
<td>30D-35°C-17</td>
<td>0.449</td>
<td>0.252</td>
<td>0.82</td>
</tr>
<tr>
<td>100D-35°C-15</td>
<td>0.455</td>
<td>0.246</td>
<td>1.85</td>
</tr>
<tr>
<td>100D-35°C-16</td>
<td>0.480</td>
<td>0.240</td>
<td>1.79</td>
</tr>
<tr>
<td>100D-35°C-17</td>
<td>0.486</td>
<td>0.248</td>
<td>10.30</td>
</tr>
</tbody>
</table>

4.4 Creep Test Results

Figure 4-8 shows the summary of creep compliance variation with time for various specimens tested at 22°C. As expected, the creep compliance and creep rate decrease as the specimen age increases.
Figures 4-9 and 4-10 show the creep test results for specimens tested at 30°C and 35°C at different ages. Compared to 22°C creep tests, the batch scatter for 7-day-old specimens is magnified as the test temperature is increased. The batch variability is most probably due to variation in the curing conditions as the experimental program was spread over a year, resulting in variation in temperature and humidity conditions under which the specimen were cured.
Figure 4-9: Summary of creep compliance versus time at 30°C

Figure 4-10: Summary of creep compliance versus time at 35°C
A sum of exponential functions as expressed in Equation 4-2 gave a good fit to the variation of creep compliance, $D$, with time ($t$) for individual creep tests done at 30°C and 35°C.

$$D = k_1 e^{k_2 t} + k_3 e^{k_4 t} \quad (4-2)$$

The creep compliance of individual specimens at 22°C could be fitted using a power law in time, as expressed in Equation 4-3.

$$D = \tau_1 t^{\tau_2} \quad (4-3)$$

The experimentally obtained results from three (five in one case) different batches were averaged out to obtain a single representative creep behavior for each test condition which is used for comparisons and for modeling the creep behavior. The testing conditions and corresponding representative creep functions are listed in Table 4-4.
Table 4-4: Average representative creep compliance functions for various test conditions

<table>
<thead>
<tr>
<th>Test Condition</th>
<th>Average Representative Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>7D-22°C</td>
<td>([(2.009) \times 10^{-5} t^{0.3885} + (1.973) \times 10^{-5} t^{0.4262} + (2.441) \times 10^{-5} t^{0.3899}] / 3 )</td>
</tr>
<tr>
<td>7D-30°C</td>
<td>([ (0.01696 e^{3.636 \times 10^{-6} t} - 0.01621 e^{-0.002158 t}) + (0.01034 e^{1.175 \times 10^{-5} t} - 0.00894 e^{-0.002317 t}) + (0.02766 e^{4.604 \times 10^{-6} t} - 0.02757 e^{-0.002441 t}) + (0.004397 e^{2.305 \times 10^{-5} t} - 0.003774 e^{-0.00125 t}) + (0.01242 e^{0.394 \times 10^{-6} t} - 0.01177 e^{-0.001629 t})] / 5 )</td>
</tr>
<tr>
<td>7D-35°C</td>
<td>([ (0.007038 e^{1.206 \times 10^{-5} t} - 0.007496 e^{-0.002276 t}) + (0.01738 e^{3.491 \times 10^{-6} t} - 0.01951 e^{-0.003665 t}) + (0.03526 e^{2.93 \times 10^{-6} t} - 0.03791 e^{-0.004408 t}] / 3 )</td>
</tr>
<tr>
<td>30D-22°C</td>
<td>([(5.234) \times 10^{-6} t^{0.4107} + (3.461) \times 10^{-6} t^{0.3894} + (1.799) \times 10^{-6} t^{0.5449}] / 3 )</td>
</tr>
<tr>
<td>30D-30°C</td>
<td>([ (0.001142 e^{6.559 \times 10^{-5} t} - 0.0005226 e^{-0.0009133 t}) + (0.003151 e^{3.647 \times 10^{-7} t} - 0.002276 e^{-0.0004637 t}) + (0.0009454 e^{0.001072 t} - 0.0004154 e^{-0.0008114 t}] / 3 )</td>
</tr>
<tr>
<td>Temperature</td>
<td>Compliance Equation</td>
</tr>
<tr>
<td>-------------</td>
<td>---------------------</td>
</tr>
</tbody>
</table>
| 30D-35°C    | \[
\begin{align*}
&{(0.002577e^{9.82(10^{-6})t} - 0.002481e^{-0.001067t})} \\
&+{(0.003164e^{-2.387(10^{-5})t} - 0.003131e^{-0.001124t})} \\
&+{(0.003604e^{1.435(10^{-5})t} - 0.003676e^{-0.001416t})}]/3
\end{align*}
\] |
| 100D-22°C   | \[
\begin{align*}
&(2.763)(10^{-7})t^{0.6717} + (2.763)(10^{-7})t^{0.6717} + (1.826)(10^{-6})t^{0.4617}]/3
\end{align*}
\] |
| 100D-30°C   | \[
\begin{align*}
&{(0.0005632e^{5.967(10^{-5})t} - 0.0001136e^{-0.0007502t})} \\
&+{(0.0009393e^{8.521(10^{-5})t} - 0.0002155e^{-0.0005697t})} \\
&+{(0.001497e^{1.595(10^{-5})t} - 0.0003608e^{-0.0001297t})}]/3
\end{align*}
\] |
| 100D-35°C   | \[
\begin{align*}
&{(0.0009423e^{5.629(10^{-5})t} - 0.0009209e^{-0.0005005t})} \\
&+{(0.001507e^{7.224(10^{-8})t} - 0.001497e^{-0.0001559t})} \\
&+{(0.01169e^{3.422(10^{-8})t} - 0.01162e^{-3.513(10^{-5})t})}]/3
\end{align*}
\] |

Time dependent deformation increases with the test temperature for specimen at a particular age. The average representative creep compliance curves for specimens tested at different temperatures at a constant initial age are shown in Figures 4-11, 4-12 and 4-13. It can be seen that creep compliance values for 7-day-old specimens crept at 30°C and 35°C are two orders of magnitude greater than specimens crept at 22°C. For 30-day-old specimens, creep compliance values are two orders of magnitude higher at 35°C and one order of magnitude higher at 30°C in comparison to creep compliance at 22°C. For 100-day-old specimens, creep compliance of specimens crept at 35°C and 30°C are an order of magnitude higher then specimen crept at 22°C.
It should be noted that the specimen is evolving while it is being tested owing to physical aging phenomena. At temperatures close to $T_g$, the rate of aging is high and the specimen is evolving at a faster rate. Hence, at a particular instant of time during the creep test, a specimen at a higher temperature would have evolved farther towards equilibrium as compared to a specimen tested at a lower temperature.

Figure 4-11: Representative creep compliance curves for 7-day-old specimens tested at 22°C, 30°C and 35°C.
As was mentioned in the description of the creep test procedure, elastic compliances were recorded 10 minutes from the start of the creep test, once the temperature reached equilibrium. Upon inversion of the elastic compliance, the elastic modulus is obtained. Thus, the recorded
elastic moduli may be artificially low versus true instantaneous elastic moduli. Table 4-5 summarizes the elastic modulus of epoxy resin characterized at various ages and test temperatures. Figure 4-14 shows age-dependent functions to predict the elastic modulus of epoxy resin at different test temperatures.

Table 4-: Elastic modulus of epoxy resin at different ages and test temperatures.

<table>
<thead>
<tr>
<th>Test condition</th>
<th>Trial 1 Elastic Modulus (MPa)</th>
<th>Trial 2 Elastic Modulus (MPa)</th>
<th>Trial 3 Elastic Modulus (MPa)</th>
<th>Trial 4 Elastic Modulus (MPa)</th>
<th>Trial 5 Elastic Modulus (MPa)</th>
<th>Average Elastic Modulus (MPa)</th>
<th>Coefficient of Variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7D-22°C</td>
<td>3130</td>
<td>3130</td>
<td>3070</td>
<td>*</td>
<td>*</td>
<td>3106</td>
<td>1.1</td>
</tr>
<tr>
<td>30D-22°C</td>
<td>3200</td>
<td>3200</td>
<td>4600</td>
<td>*</td>
<td>*</td>
<td>3669</td>
<td>22</td>
</tr>
<tr>
<td>100D-22°C</td>
<td>3860</td>
<td>3840</td>
<td>3990</td>
<td>*</td>
<td>*</td>
<td>3897</td>
<td>2.13</td>
</tr>
<tr>
<td>7D-30°C</td>
<td>905</td>
<td>769</td>
<td>846</td>
<td>1587</td>
<td>1204</td>
<td>1062</td>
<td>31.68</td>
</tr>
<tr>
<td>30D-30°C</td>
<td>1786</td>
<td>1205</td>
<td>2222</td>
<td>*</td>
<td>*</td>
<td>1737</td>
<td>29</td>
</tr>
<tr>
<td>100D-30°C</td>
<td>2222</td>
<td>2656</td>
<td>2475</td>
<td>*</td>
<td>*</td>
<td>2451</td>
<td>8.8</td>
</tr>
<tr>
<td>7D-35°C</td>
<td>719</td>
<td>775</td>
<td>971</td>
<td>*</td>
<td>*</td>
<td>821</td>
<td>16</td>
</tr>
<tr>
<td>30D-35°C</td>
<td>1050</td>
<td>1110</td>
<td>1120</td>
<td>*</td>
<td>*</td>
<td>1093</td>
<td>3.8</td>
</tr>
<tr>
<td>100D-35°C</td>
<td>1430</td>
<td>1770</td>
<td>2330</td>
<td>*</td>
<td>*</td>
<td>1841</td>
<td>24</td>
</tr>
</tbody>
</table>
4.5 Modeling Creep Response in Epoxy Resin

To model the creep response of the aging epoxy resin at different temperature a modified Findley’s power law as expressed in Equation 4-4 is used.

\[ D(t) = A(ct)^b e^{-Q/RT} \]  

(4-4)

In Equation 4-4, \( D \) is the creep compliance corresponding to creep time \( t \), \( A \) and \( b \) are the power law parameters, \( Q \) is the creep activation energy, \( R \) is the universal gas constant (8.314 J/K/mole) and \( T \) is temperature of creep test in Kelvin. The creep response is dependent on age of the specimen and test temperature. The effect of age is incorporated into the model by means of the “extent of aging” parameter (\( \beta \)). The parameters \( A \) and \( b \) are assumed to be functions of

Figure 4-14: Best-fit functions for elastic modulus of epoxy resin at various ages and temperatures
parameter $\beta$. The effect of temperature is taken into account by creep activation energy ($Q$) which itself is dependent on $\beta$.

A power law function with constant parameters $A$ and $b$ cannot be used to fit the experimental creep compliance data. Hence a modeling framework was chosen in which a power law function is used to fit experimental creep compliance data for a small range of time ($\Delta t_{fit}$) on the creep curve. The parameters of the power law ($A$ and $b$) obtained by piece-wise curve fitting can change as the creep time ($t$) varies and the specimen ages. Such a methodology is important to follow as the specimen is aging during the creep test itself and the resultant change in creep compliance can be captured using the change in power law parameters ($A$ and $b$).

To model the creep response of physically aged epoxy at different creep temperatures it is important to relate the physical aging kinetics to observed creep response using a parameter which reflects the extent of aging of the polymer. The evolution of “extent of aging” parameter ($\beta$) for different aging temperatures has been characterized in Section 3.3.2 The aging kinetics study done (Chapter 3) can also be used to determine the “equivalent age” of epoxy aged at different temperatures. Equivalent age is defined as the age at which specimens being cured at different temperatures, beyond the first 7 days of cure at room temperature, have same value of $T_g$. Figure 4-15 shows the $T_g$ evolution at different aging temperatures as discussed in Section 3.3.2. It should be noted that age here refers to the days past initial 7 days at 22°C. Equivalent age for $T_g$ value of 50°C at 22°C is 88.6 days. At 30°C, the equivalent age is 4.3 days and at 35°C it is 1.44 days. Glass transition temperature serves to relate the “extent of aging” parameter $\beta$ at different aging temperatures. For example, consider the polymer aging at 22°C temperature such that the $T_g$ has evolved to 50°C. The “extent of aging” parameter value at 22°C represented as $\beta_{22°C}$ has value of 0.994 evaluated using Equation 4-5 with $(T_{g∞})_{22°C} = 52°C$. 
If this specimen is instantaneously exposed to 30°C, \( \beta_{30^\circ C} \) calculated using Equation 4-6 will have the value 0.982, with \( (T_{g\infty})_{30^\circ C} = 56^\circ C \).

\[
\beta_{30^\circ C} = \frac{(T_g + 273)}{(T_{g\infty})_{30^\circ C} + 273}
\]  

(4-6)

In this manner, equivalent values of “extent of aging” parameter can be evaluated at different temperatures.

Figure 4-15: \( T_g \) evolution at different aging temperatures.

The creep prediction model is trained on the average experimental result for 7D-30°C creep compliance data. The test case 7D-30°C was chosen for training the model as it enabled prediction of creep during up-jump (35°C) and down-jump (22°C) temperature changes based on the available data for evaluating activation energy during aging. Also, the largest number of experimental creep tests was run at this temperature, providing the most confidence in the time
dependence of deformation. Power law functions for creep compliance in the form of Equation 4-7 are fitted to various time slices ($\Delta t_{fit}$) as shown in Figure 4-16. Time slices ($\Delta t_{fit}$) was selected to be small enough to get a good fit for Equation 4-7 but large enough to keep the modeling computationally simple.

\[ D = A(t)^b \]  \hspace{1cm} (4-7)

The variation of $\beta_{30^\circ C}$ with aging time at $30^\circ C$ is also known from results of Section 3.3.2 and has been plotted on the same plot in Figure 4-16. The fitted parameters $A$ and $b$ for different ranges of time and corresponding “extent of aging” parameter, $\beta_{30^\circ C}$ are tabulated in Table 4-6.

![Figure 4-16: Piecewise power law fitted to average representative creep compliance curve for 7-day-old specimen tested at 30°C](image)
Table 4-: Fitted creep law parameters $A$ and $b$ for different ranges of creep time and corresponding “extent of aging” parameter at 30°C

<table>
<thead>
<tr>
<th>Creep Time, $t$ (Minutes)</th>
<th>Extent of aging parameter, $\beta_{\text{SRC}}$</th>
<th>$A$</th>
<th>$b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-480</td>
<td>0.951367-0.955097</td>
<td>8.21E-05</td>
<td>0.7583</td>
</tr>
<tr>
<td>480-840</td>
<td>0.955097-0.957661</td>
<td>0.000507</td>
<td>0.4601</td>
</tr>
<tr>
<td>840-1200</td>
<td>0.957661-0.960074</td>
<td>0.001606</td>
<td>0.2884</td>
</tr>
<tr>
<td>1200-1560</td>
<td>0.960074-0.962345</td>
<td>0.003462</td>
<td>0.1798</td>
</tr>
<tr>
<td>1560-1920</td>
<td>0.962345-0.964483</td>
<td>0.005604</td>
<td>0.1142</td>
</tr>
<tr>
<td>1920-2280</td>
<td>0.964483-0.966496</td>
<td>0.007478</td>
<td>0.07596</td>
</tr>
<tr>
<td>2280-2640</td>
<td>0.966496-0.96839</td>
<td>0.008548</td>
<td>0.0586</td>
</tr>
<tr>
<td>2640-3000</td>
<td>0.96839-0.970173</td>
<td>0.009494</td>
<td>0.04522</td>
</tr>
<tr>
<td>3000-3360</td>
<td>0.970173-0.971852</td>
<td>0.01002</td>
<td>0.03850</td>
</tr>
<tr>
<td>3360-3720</td>
<td>0.971852-0.973432</td>
<td>0.01025</td>
<td>0.03568</td>
</tr>
<tr>
<td>3720-4080</td>
<td>0.973432-0.974919</td>
<td>0.01029</td>
<td>0.03514</td>
</tr>
<tr>
<td>4080-4440</td>
<td>0.974919-0.976319</td>
<td>0.01022</td>
<td>0.03594</td>
</tr>
<tr>
<td>4440-4800</td>
<td>0.976319-0.977637</td>
<td>0.01009</td>
<td>0.03754</td>
</tr>
<tr>
<td>4800-5160</td>
<td>0.977637-0.978878</td>
<td>0.009912</td>
<td>0.03963</td>
</tr>
<tr>
<td>5160-5520</td>
<td>0.978878-0.980046</td>
<td>0.009712</td>
<td>0.04201</td>
</tr>
<tr>
<td>5520-5880</td>
<td>0.980046-0.981145</td>
<td>0.0095</td>
<td>0.04458</td>
</tr>
<tr>
<td>5880-6240</td>
<td>0.981145-0.98218</td>
<td>0.009281</td>
<td>0.04727</td>
</tr>
<tr>
<td>$t &gt; 6240$</td>
<td>0.98218-1</td>
<td>0.00906</td>
<td>0.05003</td>
</tr>
</tbody>
</table>

The creep compliance prediction at 30°C, $D_{30°C}$ can be transformed to creep compliance prediction at another temperature $T$ via the creep activation energy $Q$, as expressed in Equation (4-8).

$$D_T = D_{30°C} \left( \frac{e^{-Q/(R(T+273))}}{e^{-Q/(R(30+273))}} \right) \quad (4-8)$$
The creep activation energy is assumed to depend on the “extent of aging” parameter and is modeled accordingly.

To determine $Q$, the logarithm of the creep law (Equation 4-4) is taken.

$$\ln(D_T) = \ln(A) + b\ln(t) - \left(\frac{Q}{RT}\right) \quad (4-9)$$

The value of $(-Q/R)$ can be found by plotting $\ln(D_T)$ against $(1/T)$ and choosing creep compliance values at a constant value of $\beta$ from creep tests done at 7 days age at different temperatures—i.e., 22°C, 30°C and 35°C. By choosing $D_T$ values at a constant value of $\beta$, parameters $A$ and $b$ are fixed. The percentage change in the term $\ln(t)$ for the same value of $\beta$ at different temperatures is small enough to make the term $[\ln(A)+b\ln(t)]$ nearly constant and the variation of $\ln(D_T)$ with $(1/T)$ a linear relation. Using creep compliance values at constant $\beta$ also facilitates the evaluation of $Q$ as a function of $\beta$. Figure 4-17 shows an example of points picked at the same value of $\beta$ ($\beta=0.965$) at different temperatures. From these points, the values of $\ln(t)$ at temperatures of 22°C, 30°C and 35°C are 7.4, 7.7 and 8.8, respectively. Using Table 4-6, the values of $[\ln(A)+b\ln(t)]$ are -4.22, -4.31 and -4.33 at temperatures of 22°C, 30°C and 35°C, respectively. Therefore the change in the value of $[\ln(A)+b\ln(t)]$ is approximately 0.1 while the changes in $\ln(D_T)$ and $(Q/RT)$ are approximately 3, which allows the assumption that $[\ln(A)+b\ln(t)]$ is a constant with varying temperature for a given value of $\beta$. 
Since the \( T_g \) and resulting value of \( \beta \) change very slowly with time at 22°C, the 7D-22°C representative creep compliance curve had to be extrapolated using the corresponding equation from Table 4-4 to determine creep compliances at similar values of \( \beta \) as used in the higher two temperatures. Figure 4-18 shows the plot of \( \ln(D_T) \) against \( (1/T) \) made by picking points at same value of \( \beta \) at different temperatures, as discussed above. The figure also shows the linear functions fitted to the three temperatures corresponding to a particular value of \( \beta \). The slope of each plot represents the value of \( Q/R \) corresponding to selected values of \( \beta \).
The variation of $Q/R$ with values of “extent of aging” parameter $\beta$ is shown in Figure 4-19. A few fictitious points (encircled), with assignment based on the observed trend, were added at very low and high values of $\beta$ to cover the entire range of $\beta$ observed during all the creep tests. A power law expressed in Equation 4-10 was used to fit this data.

$$\frac{Q}{R} = 14826\beta^{-14} \quad (4-10)$$

where the units of $Q/R$ are Kelvin.
Equipped with the knowledge of evolution of $\beta$ at three different temperatures, the dependence of creep power law parameters $A$ and $b$ on $\beta_{30^\circ C}$ and the transformation of creep compliance at $30^\circ C$ to creep compliance at other temperatures using the $\beta$-dependent thermal activation energy, an attempt to model creep behavior in epoxy at different ages and creep temperatures was made. A MATLAB® based computer code *Creepmodeling* (Appendix C) was developed for this purpose. The modeling framework has been shown in form of a flowchart in Figure 4-20. The user inputs the creep temperature ($T$), aging time at $22^\circ C$ ($t_a$) and creep duration ($t$). Although the initial $\beta$ could be evaluated for various initial aging temperatures prior to creep, the model is currently written for initial aging at $22^\circ C$. 

Figure 4-19: Variation of $(Q/R)$ with “extent of aging” parameter $\beta$
Using the methodology discussed above, before the start of a creep test, the equivalent age at 30°C ($t_{a30°C}$) and equivalent $\beta$ at 30°C ($\beta_{30°C}$) are calculated for aging time at 22°C ($t_a$). For the creep duration ($t$), the code iteratively evaluates the “extent of aging” parameter ($\beta_{30°C}$) based on the aging map at 30°C and corresponding values of creep power law parameters $A$ and $b$ (using Table 4-6). The evolution of $\beta_{30°C}$ starts with the initial value of $\beta_{30°C}$ and evolves as the $T_g$ evolves at 30°C (Figure 4-15). The creep compliance ($D_{30°C}$) at time $t$, for $t_a$ greater than 7 days is calculated as expressed in Equation (4-11).

$$D_{30°C}(t) = A(t + t_{a30°C})^m - A_i(t_{a30°C})^{m_i}$$

(4-11)

where $A_i$ and $m_i$ are values of $A$ and $m$ corresponding to initial value of aging parameter ($\beta_{i30°C}$).

It can be seen that the creep compliance function depends on the instantaneous value of “extent of aging” parameter ($\beta_{30°C}$), initial age ($t_{a30°C}$) and “extent of aging” parameter of the material prior to creep loading ($\beta_{i30°C}$).

Depending upon the creep temperature ($T$), creep compliance at 30°C ($D_{30°C}$) can be transformed to creep compliance at temperature $T$ ($D_T$) using Equation 4-8. The values of $\beta$ are evaluated iteratively depending on creep temperature $T$ using the aging map at different temperatures from Figure 4-15. Then, the creep activation energy ($Q$), which depends on $\beta$, is evaluated. Thus, the temperature-dependent time evolution in creep activation energy is evaluated by Equation 4-10, which is in turn used in Equation 4-8 to evaluate $D_T$. 
Figure 4-20: Creep prediction flowchart

- Evaluate $\beta_{30°C}(t)$ and $A_{30°C}$ and $m_{30°C}$
- If $T = 30°C$
  - Initialize $t' = 0$
  - Plot $D_T$ vs time ($t$)
  - $D_T(t) = D_{30°C}(t)$

- If $t' < t$
  - Evaluate $\beta(t')$, $Q(t')$, and $D_T$

- Initialize $t = 0$
- Evaluate $D_{30°C}(t)$
  - If $t < t'$
  - Initialize $t' = 0$

- Input aging time at 22°C ($t_a$), creep temperature ($T$), and creep duration ($t$) in minutes

- Input creep duration ($t$) in minutes

- Input creep duration ($t$) and creep duration ($t$) in minutes
The results for creep compliance prediction in epoxy specimen at age of 30 and 100 days and creep temperatures of 22°C, 30°C and 35°C have been summarized in Figures 4-21 to 4-26 along with corresponding bands of experimental scatter. The creep model predicts the creep compliance behavior within the experimental scatter for most of the cases. The model prediction for 30D-35°C was not realistic as a slight decrease in creep compliance was observed in between 1000 to 3000 minutes. At greater times, however, the correct creep compliance rate is captured.

Figure 4-21: Model prediction for creep of 30D-22°C specimen
Figure 4-22: Model prediction for creep of 30D-30°C specimen

Figure 4-23: Model prediction for creep of 30D-35°C specimen
Figure 4-24: Model prediction for creep of 100D-22°C specimen

Figure 4-25: Model prediction for creep of 100D-30°C specimen
4.6 Conclusion

Tensile creep characteristics of epoxy resin coupons were studied at the ages of 7, 30 and 100 days and creep temperatures of 22°C, 30°C and 35°C. As material aged, it became stiffer and its creep compliance and creep rate decreased. The knowledge of physical aging kinetics was utilized to link the mechanically observed creep behavior to the newly proposed “extent of aging” parameter ($\beta$). The novelty of this technique is in the ease with which aging can be characterized for a complex thermal history of polymer which governs its creep behavior. The advantage of using this technique over preceding techniques to model non-isothermal aging is that creep response is not derived from parameters of a structural recovery model but a more tangible experimentally measured quantity (glass transition temperature). A MATLAB code was developed based on this technique to predict the creep behavior of resin aged at 22°C for a variable time and then subjected to creep loading at different temperatures. The predictions of the analytical model were mostly in good agreement with the experimentally observed creep behavior, especially in capturing creep rate trends at creep times greater than 3000 minutes (50 hours).
Chapter 5
Conclusions and Recommendations for Future Work

5.1 Conclusions

The present investigation introduces a methodology for experimentally and theoretically characterizing age- and temperature-dependent creep behavior in a representative epoxy resin that is used for strengthening civil structures and which cures in ambient temperature conditions.

In the first phase of the investigation, the glass transition temperature ($T_g$) of the resin cured and aged at 22°C was characterized using dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) at ages of 7, 30 and 100 days. The results showed a dependence of $T_g$ on the method used to assign $T_g$. Based on DMA scans, $T_g$ was assigned using the variation of storage modulus, loss modulus and Tan δ with temperature. DSC thermograms were used to assign $T_g$ at the onset of glass transition. The results showed a precariously low value of $T_g$ around 40°C at the age of 7 days which can limit the elevated temperature capability of the structure. An increase in $T_g$ of almost 15°C was observed between a 7-day-old resin specimen and a specimen aged 100 days at room temperature, based on the dynamic storage modulus.

In the second phase of the investigation, the kinetics of chemical cure and physical aging of the selected epoxy were studied using the DSC technique. An isoconversion map to predict evolution of degree of cure ($\alpha$) was developed. This map was used to conclude that no evolution in degree of cure ($\alpha$) takes place at aging temperatures up to 70°C following 7 days of curing at
Further, DSC experiments established that physical aging (structural relaxation) towards material equilibrium was the cause for the increase in $T_g$ observed at 22°C. To systematically study the kinetics of physical aging, resin was aged at 30°C and 35°C and the evolution of $T_g$ with aging time was measured. An aging map, based on evolution of $T_g$ with age at three different temperatures—22°C, 30°C and 35°C—was constructed for use in modeling the kinetics of physical aging. An “extent of aging” parameter ($\beta$) was defined in terms of the easily-measured $T_g$ to parametrize the evolution of material toward equilibrium.

The third phase of the investigation involved experimental creep measurements and analytical modeling of the creep behavior based on specimen age and creep conditions. Tensile creep compliance was measured in the resin at the ages of 7, 30 and 100 days at three different temperatures—22°C, 30°C and 35°C. Creep compliance and the creep rate decreased with increasing age of the material. The observed mechanical creep behavior was linked to the “extent of aging” parameter ($\beta$) developed earlier and to the creep test temperature via a creep activation energy ($Q$). The analytical model was used to predict creep in resin specimen undergoing non-isothermal aging. The modeling approach adopted was successful in capturing the evolution in material behavior during the creep test. The modeling results were in good agreement with experimental results for most of the experimental test cases, particularly in capturing the creep rate beyond 50 hours.

5.1 Recommendations and Scope for Future Work

- One of the keys to consistent material behavior of ambient temperature cured resin is to maintain very tight control over temperature and humidity during molding and aging of
the resin. The scatter in the experimental creep results can be reduced if a climate control chamber is used.

- Owing to time constraints, the development of the aging map was based on DSC scans on only one batch of resin. DSC scans on multiple batches of resin following the same test procedure will make the aging map more reliable and possibly improve the results of creep prediction model.

- Creep behavior was assumed to be linear in stress in the modeling effort. This assumption should be checked by running additional experiments at different stress levels.

- The shear creep in fiber-reinforced composite laminates should also be investigated. This type of creep could be an important contributor to the total creep deformation of a structure strengthened with FRP laminate.

- There is a need to develop an ambient temperature cured resin system with improved elevated temperature behavior—i.e., high $T_g$ and low creep rate at elevated temperature. Nanoscale reinforcements such as nanosilica, polyhedral oligomeric silsesquioxanes (POSS), carbon nanofibers and nanotubes may be used to enhance the $T_g$ and mechanical properties at elevated temperatures.
The civil infrastructure design guidelines for repair and strengthening using FRP externally bonded reinforcements (such as ACI 440-2R-08 [12] and fib Bulletin 14 [6]) need to be amended in terms of guidelines for characterizing the $T_g$ of the employed resins and the elevated temperature capability of strengthened structures. There is a need to define a standard test method for assigning $T_g$ with specific details on curing conditions of the resin and test parameters, as the $T_g$ assigned is highly dependent on them. Research is needed to characterize the residual strength of structures strengthened with FRP and subjected to various sustained loads and various elevated temperatures. Based on these amendments and research findings, improved guidelines for the safe design of strengthened structures can be realized.

The effect of humidity on the aging kinetics of epoxy resin and creep behavior of epoxy resin should be studied and modeled. Design guidelines for structures subjected to wet conditions should reflect these findings.
References


Appendix A

Detailed Experimental Results

DMA Results: 7-Day-Old-Storage Modulus

7A: Storage Modulus vs. Temperature

7B: Storage Modulus vs. Temperature

7C: Storage Modulus vs. Temperature
DMA Results: 7-Day-Old-Loss Modulus

### 7A: Loss Modulus vs. Temperature

![Graph showing Loss Modulus vs. Temperature for Run 1, Run 2, and Run 3. Peaks at TgR1=50°C, TgR2=67°C, TgR3=75°C.](image)

### 7B: Loss Modulus vs. Temperature

![Graph showing Loss Modulus vs. Temperature for Run 1, Run 2, and Run 3. Peaks at TgR1=49°C, TgR2=67°C, TgR3=76°C.](image)

### 7C: Loss Modulus vs. Temperature

![Graph showing Loss Modulus vs. Temperature for Run 1, Run 2, Run 3, Run 4, Run 5, Run 6. Peaks at TgR1=44°C, TgR2=66°C, TgR3=74°C, TgR4=78°C, TgR5=79°C, TgR6=80°C.](image)
DMA Results: 7-Day-Old-Tan $\delta$

### 7A: Tan $\delta$ vs. Temperature

![Graph A](image)

- $T_{gR1} = 59$° C
- $T_{gR3} = 82$° C
- $T_{R2} = 75$° C

### 7B: Tan $\delta$ vs. Temperature

![Graph B](image)

- $T_{gR1} = 60$° C
- $T_{gR2} = 85$° C
- $T_{gR3} = 92$° C

### 7C: Tan $\delta$ vs. Temperature

![Graph C](image)

- $T_{gR1} = 57$° C
- $T_{gR2} = 84$° C
- $T_{gR3} = 91$° C
- $T_{gR4} = 93$° C
- $T_{gR5} = 94$° C
- $T_{gR6} = 95$° C
DMA Results: 30-Day-Old-Storage Modulus

30A: Storage Modulus vs. Temperature

30B: Storage Modulus vs. Temperature

30C: Storage Modulus vs. Temperature

Run 1
Run 2
Run 3

TgR1=51°C
TgR2=63°C
TgR3=66°C

TgR1=51°C
TgR2=53°C
TgR3=59°C
TgR4=63°C
TgR5=64°C
TgR6=66°C

TgR1=48°C
TgR2=51°C
TgR3=59°C
TgR4=60°C
TgR5=65°C
TgR6=66°C
DMA Results: 30-Day-Old-Loss Modulus

30A: Loss Modulus vs. Temperature

30B: Loss Modulus vs. Temperature

30C: Loss Modulus vs. Temperature
DMA Results: 30-Day-Old-Tan $\delta$
DMA Results: 100/130-Day-Old-Storage Modulus

100A: Storage Modulus vs. Temperature

100B: Storage Modulus vs. Temperature

130A: Storage Modulus vs. Temperature
DMA Results: 100/130-Day-Old-Loss Modulus

100A: Loss Modulus vs. Temperature

100B: Loss Modulus vs. Temperature

130A: Loss Modulus vs. Temperature
DMA Results: 100/130-Day-Old-Tan δ

100A: Tan δ vs. Temperature

100B: Tan δ vs. Temperature

130C: Tan δ vs. Temperature
DMA Results: 30-Day Moisture Soaked Storage Modulus

30A_b: Storage Modulus vs. Temperature

30B_b: Storage Modulus vs. Temperature

30C_b: Storage Modulus vs. Temperature
DMA Results: 30-Day Moisture Soaked Loss Modulus

30A_h: Loss Modulus vs. Temperature

30B_h: Loss Modulus vs. Temperature

30C_h: Loss Modulus vs. Temperature
DMA Results: 30-Day Moisture Soaked Tan $\delta$

30A\textsubscript{h}: Tan $\delta$ vs. Temperature

30B\textsubscript{h}: Tan $\delta$ vs. Temperature

30C\textsubscript{h}: Tan $\delta$ vs. Temperature
DMA Results: 100-Day Moisture Soaked Storage Modulus

100Aₜ: Storage Modulus vs. Temperature

100Bₜ: Storage Modulus vs. Temperature

100Cₜ: Storage Modulus vs. Temperature
DMA Results: 100-Day Moisture Soaked Loss Modulus

100A<sub>i</sub>: Loss Modulus vs. Temperature

100B<sub>i</sub>: Loss Modulus vs. Temperature

100C<sub>i</sub>: Loss Modulus vs. Temperature
DMA Results: 100-Day Moisture Soaked Tan δ

100A: Tan δ vs. Temperature

100B: Tan δ vs. Temperature

100C: Tan δ vs. Temperature
DSC Results: 7-Day-Old

**DSC scan 7A'**

- Tg Run1 = 58°C, Tg Run2 = 61°C
- Tg Run1 = 40°C, Tg Run2 = 65°C

**DSC scan 7B'**

- Tg Run1 = 55°C, Tg Run2 = 63°C
- Tg Run1 = 40.8°C, Tg Run2 = 69°C

**DSC scan 7C'**

- Tg Run1 = 40.03°C
DSC Results: 30-Day-Old

DSC scan 30A'

DSC scan 30B'

DSC scan 30C'
DSC Results: 100-Day-Old

DSC scan 100A°

DSC scan 100B°

DSC scan 100 C°
Creep Test: 7D-35°C

7D-35°C-15

7D-35°C-16

7D-35°C-17
Creep Test: 30D-35°C

30D-35°C-15

30D-35°C-16

30D-35°C-17
Creep Test: 100D-35°C

100D-35°C-15

100D-35°C-16

100D-35°C-17
Creep Test: 7D-30°C

**Graphs:**

- **7D-30°C-10**
  - Graph showing strain vs. time for Extensometer A, Extensometer B, and Average.
  - Time range: 0 to 6000 minutes.

- **7D-30°C-11**
  - Graph showing strain vs. time for Extensometer A, Extensometer B, and Average.
  - Time range: 0 to 6000 minutes.

- **7D-30°C-12**
  - Graph showing strain vs. time for Average, Strain A, and Strain B.
  - Time range: 0 to 8000 minutes.

- **7D-30°C-13**
  - Graph showing strain vs. time for Average, Strain A, and Strain B.
  - Time range: 0 to 8000 minutes.

- **7D-30°C-14**
  - Graph showing strain vs. time for Average, Strain A, and Strain B.
  - Time range: 0 to 8000 minutes.
Creep Test: 30D-30°C

<table>
<thead>
<tr>
<th>Time (Minutes)</th>
<th>Strain A</th>
<th>Strain B</th>
<th>Average Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.0005</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>1000</td>
<td>0.0005</td>
<td>0.0010</td>
<td>0.00075</td>
</tr>
<tr>
<td>2000</td>
<td>0.0015</td>
<td>0.0020</td>
<td>0.00175</td>
</tr>
<tr>
<td>3000</td>
<td>0.0020</td>
<td>0.0025</td>
<td>0.00225</td>
</tr>
<tr>
<td>4000</td>
<td>0.0025</td>
<td>0.0030</td>
<td>0.00275</td>
</tr>
<tr>
<td>5000</td>
<td>0.0030</td>
<td>0.0035</td>
<td>0.00325</td>
</tr>
<tr>
<td>6000</td>
<td>0.0035</td>
<td>0.0040</td>
<td>0.00375</td>
</tr>
</tbody>
</table>
Creep Test: 100D-30°C

100D-30°C-10

100D-30°C-12

100D-30°C-13
Creep Test: 7D-22°C

**7D-22°C-1**

![Graph of Strain vs. Time for 7D-22°C-1](image)

**7D-22°C-2**

![Graph of Strain vs. Time for 7D-22°C-2](image)

**7D-22°C-3**

![Graph of Strain vs. Time for 7D-22°C-3](image)
Creep Test: 30D-22°C

30D-22°C-4

30D-22°C-5

30D-22°C-6

Strain

Time (Minutes)

Strain A

Strain B

Average Strain

Strain

Time (Minutes)
Creep Test: 100D-22°C

100D-22°C-7

Strain vs. Time (Minutes)

100D-22°C-8

Strain vs. Time (Minutes)

100D-22°C-9

Strain vs. Time (Minutes)
Appendix B

Validation of Time-Aging Time Superposition

Specimens from Batch 3 were tested at ages of 3, 5 and 7 days to verify the time-aging time superposition as explained by Struiik (1977) [24]. The momentary creep response for the specimen tested at the age of 3, 5 and 7 days—i.e., the creep response for the duration of one-tenth of the aging time ($t_a/10$)—was utilized to create a master curve for a 7-day-old epoxy specimen. The momentary creep response for epoxy at the age of 3 and 5 days were horizontally shifted on the log($t$) scale to superimpose the momentary creep response of 7-day-old epoxy specimen as shown in Figure (B1).

![Figure B1: Master creep curve for 7D-22°C-2 specimen.](image)

The plot of horizontal shift factor (log $a$) and ageing time (log $t_a$) also follows the observation of Struiik (1977) that creep curves shift at a constant rate with aging time as shown in Figure (B2).
Figure B2: Logarithm of aging time and horizontal shift showing the constant rate of increase of shift factor.
Appendix C

Matlab Code Creepmodeling

clear all;
close all;
clc;

syms t
%user input ta & T
ta=7;
T=22;
%Evaluation of eqage_30 & eqbeta_30

Tg_rt=40.46+(52-40.4606)*(((ta-7)^2)/(40.7625^2+(ta-7)^2))
f=55.58*exp(2.963*10^-5*t)-15.56*exp(-0.2421*t)-Tg_rt;
g=59.9*exp(8.816*10^-6*t)-19.77*exp(-0.4689*t)-Tg_rt;
eqage_30=double(solve(f))
eqage_35=double(solve(g))
eqbeta_30=double((55.58*exp(2.963*10^-5*eqage_30)-15.56*exp(-
0.2421*eqage_30)+273)/(56+273))
i=1;
if ta==7
    eqage_30=0
end
%evaluate creep parameter using eqbeta_30
for ct=1:10:5000
    beta(ct)=double(((55.58*exp(2.963*10^-5*(eqage_30+(ct/60/24)))-
    15.56*exp(-0.2421*(eqage_30+(ct/60/24)))+273))/(56+273));
    if double(beta(ct))<0.955097
        a(ct)=8.21*10^-5;
b(ct)=0.7583;
    end
    if double(beta(ct))>0.955097 & double(beta(ct))<=0.957661
        a(ct)=0.000507;
b(ct)=0.4601;
    end
    if double(beta(ct))>0.957661 & double(beta(ct))<=0.960074
        a(ct)=0.001606;
b(ct)=0.2884;
    end
    if double(beta(ct))>0.960074 & double(beta(ct))<=0.962345
        a(ct)=0.003462;
b(ct)=0.1798;
if double(beta(ct)) > 0.962345 && double(beta(ct)) <= 0.964483
    a(ct) = 0.005604;
    b(ct) = 0.1142;
end
if double(beta(ct)) > 0.964483 && double(beta(ct)) <= 0.966496
    a(ct) = 0.007478;
    b(ct) = 0.07596;
end
if double(beta(ct)) > 0.966496 && double(beta(ct)) <= 0.96839
    a(ct) = 0.008548;
    b(ct) = 0.0586;
end
if double(beta(ct)) > 0.96839 && double(beta(ct)) <= 0.970173
    a(ct) = 0.009494;
    b(ct) = 0.04522;
end
if double(beta(ct)) > 0.970173 && double(beta(ct)) <= 0.971852
    a(ct) = 0.01002;
    b(ct) = 0.0385;
end
if double(beta(ct)) > 0.971852 && double(beta(ct)) <= 0.973432
    a(ct) = 0.01025;
    b(ct) = 0.03568;
end
if double(beta(ct)) > 0.973432 && double(beta(ct)) <= 0.974919
    a(ct) = 0.01029;
    b(ct) = 0.03514;
end
if double(beta(ct)) > 0.974919 && double(beta(ct)) <= 0.976319
    a(ct) = 0.01022;
    b(ct) = 0.03594;
end
if double(beta(ct)) > 0.976319 && double(beta(ct)) <= 0.977637
    a(ct) = 0.010919;
    b(ct) = 0.03754;
end
if double(beta(ct)) > 0.977637 && double(beta(ct)) <= 0.978878
    a(ct) = 0.009912;
    b(ct) = 0.04201;
end
if double(beta(ct)) > 0.978878 && double(beta(ct)) <= 0.980046
    a(ct) = 0.009712;
    b(ct) = 0.04458;
end
if double(beta(ct)) > 0.980046 && double(beta(ct)) <= 0.981145
    a(ct) = 0.0095;
    b(ct) = 0.04727;
end
if double(beta(ct)) > 0.981145 && double(beta(ct)) <= 0.98218
    a(ct) = 0.009281;
    b(ct) = 0.049727;
end
if double(beta(ct)) > 0.98218 && double(beta(ct)) < 1
    a(ct) = 0.00906;
    b(ct) = 0.05003;


time(i)=ct;
    betatest(i)=beta(ct);
%atest(i)=a(ct);
%btest(i)=b(ct);

cc(i)=a(ct)*(ct+(eqage_30*24*60))^b(ct)-(a(1)*(eqage_30*24*60)^b(1));
%cc(i)=a(ct)*(ct+(eqage_30*24*60))^b(ct);

if T==30
    alpha(ct)=double(((55.58*exp(2.963*10^-5*(eqage_30+(ct/60/24)))-
                      15.56*exp(-0.2421*(eqage_30+(ct/60/24)))+273))/(56+273));
end
if T==22
    alpha(ct)=((40.46+(52-40.4606)*(((ta-7+(ct/60/24))^2)/(40.7625^2+((ta-
                      7+(ct/60/24)))^2)))+273)/(52+273);
end
if T==35
    alpha(ct)=double(((59.9*exp(8.816*10^-6*(eqage_35+(ct/60/24))))-
                      19.77*exp(-0.4689*((eqage_35+(ct/60/24))))+273)/(60+273));
end

%Evaluation of creep activation energy

q(i)=5903*(double(alpha(ct)))^-24.9+10310;

cc(i)=cc(i)*exp(-1*q(i)/(T+273))/exp(-1*(q(i)/(30+273)));

i=i+1;
end

s=transpose(cc);
%p=transpose(atest);
%q=transpose(btest);
%r=transpose(betatest);
x=1:10:5000;
%plot(x,r)
%plot(r,p)
%plot(r,q)

plot(x,cc)
hold on
%plot(t_30_7,cc_30_7)
%plot(t_30_30,cc_30_30)
%plot(t_35_30, cc_35_30)
%plot(t_30_100, cc_30_100)
%plot(t_RT_30, cc_RT_30)
plot(t_RT_7, cc_RT_7)
%plot(t_RT_100, cc_RT_100)
%plot(t_35_100, cc_35_100)
%plot(t_35_7, cc_35_7)
Appendix D

Thermoreversibility of Physical Aging

Physical aging is a thermoreversible process. The effects of physical aging can be erased by exposing a specimen to a temperature above its glass transition temperature. To check the thermoreversibility of physical aging in the epoxy resin under study, a DSC test program was devised. A resin sample cured at 22°C for 7 days was used in this investigation. The resin sample was subjected to temperature slightly above its $T_g$ by heating it upto 50°C at 3°C/min from 0°C to 50°C and then quickly cooling it to 0°C in an uncontrolled manner. Another scan at the rate of 3°C/min was done on the resin sample to check if the endothermic relaxation peak, which is present due to physical aging, was erased. As seen in Figure D1, during the first scan an endothermic relaxation peak indicating physical aging in 7-day-old sample was observed. The $T_g$ of sample was 42°C. During the second scan (Figure D2) no endothermic relaxation peak was observed but the glass transition temperature was 43°C, close to $T_g$ value during the first scan. Thus, it was observed (Figure D1 and Figure D2) that after exposing the resin to temperature above its $T_g$ the effect of physical aging was erased but the glass transition was approximately the same. It is expected that with the erasure of physical aging the $T_g$ should decrease. But as the specimen tested were only 7-day-old, the effect of physical aging was not significant enough to influence the $T_g$ of the resin.
Figure D1: First DSC scan showing the presence of physical aging in resin

Figure D2: Second DSC scan after exposing the specimen to temperature above its $T_g$