

PROCESS OPTIMIZATION OF AUTOCLAVE BONDED LIGHT-WEIGHT  
MATERIAL JOINTS

by

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*To my father*

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Shraddha Ratnakar Jagatap



## ABSTRACT

### PROCESS OPTIMIZATION OF AUTOCLAVE BONDED LIGHT-WEIGHT MATERIAL JOINTS

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Adviser: Sayed Nassar, Ph.D.

This dissertation research fills a gap in the existing open literature regarding the significance of autoclave cure process variables and their interactions on the static strength of lightweight material single lap joints under tensile-shear loading. Specifically, the research investigates the dependence between the degree of cure of the epoxy adhesive and the mechanical performance of the single lap joint bonded with same epoxy adhesive.

Lightweight material system includes polycarbonate, Aluminum 6061 and glass reinforced plastics (GFRP) extren 500. A commercially available polyurethane film adhesive PE399 was selected to bond Polycarbonate single lap joints (SLJ) while epoxy film adhesive AF163-2K was selected to bond aluminum and GFRP joints. Studied variables include cure temperature, cure pressure and their respective rates as well as the duration of cure time.

Dynamic Mechanical Analysis (DMA) is used to quantify glass transition temperature of AF163-2K cured with different combinations of autoclave process variables. The relative significance of variables and variable combinations are

investigated for their effect on the bond strength. Experimental test data shows interaction between autoclave variable cure temperature in combination with cure time, temp ramp rate and pressure ramp rate have significant effect on glass transition temperature, bond strength and failure mode. Changes in joint static load transfer capacity (LTC) was investigated after cyclic temperature profile fluctuates between 20° C and 85° C at a constant relative humidity (RH) level of 85 %.

## TABLE OF CONTENTS

|                                                         |     |
|---------------------------------------------------------|-----|
| ACKNOWLEDGMENTS                                         | iv  |
| ABSTRACT                                                | v   |
| LIST OF TABLES                                          | x   |
| LIST OF FIGURES                                         | xi  |
| LIST OF ABBREVIATIONS                                   | xvi |
| <br>CHAPTER ONE                                         |     |
| INTRODUCTION AND LITERATURE SURVEY                      | 1   |
| 1.1 General Overview                                    | 1   |
| 1.2 Lightweight Solutions                               | 4   |
| 1.3 Literature Survey                                   | 7   |
| 1.3.1 Adhesive Joints                                   | 7   |
| 1.3.2 Adhesive Characterization                         | 9   |
| 1.4 Organization of Dissertation                        | 16  |
| <br>CHAPTER TWO                                         |     |
| POLYCARBONAE BONDED JOINTS WITH POLYURETHAN<br>ADHESIVE | 19  |
| 2.1 Introduction                                        | 19  |
| 2.2 Materials                                           | 19  |
| 2.3 Joining Procedures                                  | 21  |
| 2.4 Experimental Procedure and Test Setup               | 25  |
| 2.4.1 Baseline Static Load Transfer Capacity (LTC)      | 28  |
| 2.4.2 Environmental Cycling                             | 32  |

## TABLE OF CONTENTS—Continued

|                                                                   |    |
|-------------------------------------------------------------------|----|
| 2.5 ANOVA                                                         | 37 |
| CHAPTER THREE                                                     |    |
| EPOXY ADHESIVE CHARACTERIZATION                                   | 42 |
| 3.1 Introduction                                                  | 42 |
| 3.2 Epoxy Film Adhesive                                           | 42 |
| 3.3 Curing of Film Adhesive AF163-2K                              | 42 |
| 3.4 Defining Stages of Cure                                       | 46 |
| 3.5 The Glass Transition Temperature ( $T_g$ ); Indicator of Cure | 48 |
| 3.5.1 Relationship Between $T_g$ and Degree of Cure ( $\alpha$ )  | 50 |
| 3.6 experimental Procedure and Test Setup                         | 51 |
| 3.6.1 DMA Sample Preparation                                      | 51 |
| 3.6.2 Measurement of $T_g$ using DMA                              | 51 |
| 3.6.3 Glass Transition Temperature at Full Conversion             | 55 |
| 3.7 Results and Discussion                                        | 57 |
| 3.8 Effect of Cure Pressure                                       | 61 |
| 3.9 ANOVA                                                         | 63 |
| CHAPTER FOUR                                                      |    |
| ALUMINUM BONDED JOINTS WITH EPOXY ADHESIVE                        | 68 |
| 4.1 Introduction                                                  | 68 |
| 4.2 Materials                                                     | 68 |
| 4.3 Joining Procedure                                             | 69 |
| 4.4 Experimental Procedure and Test Setup                         | 70 |

## TABLE OF CONTENTS—Continued

|                                                    |     |
|----------------------------------------------------|-----|
| 4.5 Results and Discussion                         | 71  |
| 4.5.1 Baseline Static Load Transfer Capacity (LTC) | 71  |
| 4.5.2 Environmental Cycling                        | 77  |
| 4.6 ANOVA                                          | 78  |
| CHAPTER FIVE                                       |     |
| GFRP BONDED JOINTS WITH EPOXY ADHESIVE             | 83  |
| 5.1 Introduction                                   | 83  |
| 5.2 Materials                                      | 83  |
| 5.3 Joining Procedure                              | 83  |
| 5.4 Experimental Procedure and Test Setup          | 85  |
| 5.4.1 Baseline Static Load Transfer Capacity (LTC) | 85  |
| 5.4.2 Environmental Cycling                        | 85  |
| 5.5 Results and Discussion                         | 86  |
| 5.5.1 Baseline Static Load Transfer Capacity (LTC) | 86  |
| 5.5.2 Environmental Cycling                        | 91  |
| 5.6 ANOVA                                          | 91  |
| CHAPTER SIX                                        |     |
| CONCLUSION                                         | 98  |
| CHAPTER SEVEN                                      |     |
| FUTURE WORK                                        | 100 |
| REFERENCES                                         | 101 |
| PUBLICATIONS                                       | 108 |

## LIST OF TABLES

|           |                                                                          |    |
|-----------|--------------------------------------------------------------------------|----|
| Table 1.1 | Weight reduction by lightweight material                                 | 6  |
| Table 2.1 | Polycarbonate adherend mechanical properties                             | 20 |
| Table 2.2 | Polyurethane Adhesive Mechanical Properties                              | 21 |
| Table 2.3 | Autoclave Bonding Process Variable Level                                 | 23 |
| Table 2.4 | Autoclave Bonding Process Combinations                                   | 24 |
| Table 2.5 | Joint Visual Inspection for Two Level of Cure Temperature Bonded Coupons | 34 |
| Table 2.6 | ANOVA Data for Baseline Static LTC of Polycarbonate Joints               | 38 |
| Table 3.1 | Epoxy Film Adhesive AF163-K Properties                                   | 43 |
| Table 3.2 | ANOVA Data for Glass Transition Temperature ( $T_g$ )                    | 65 |
| Table 4.1 | Aluminum Adherend Mechanical Properties                                  | 68 |
| Table 4.2 | ANOVA Data for Baseline Static LTC of AL Joints                          | 79 |
| Table 5.1 | GFRP Adherend Mechanical Properties                                      | 84 |
| Table 5.2 | ANOVA Data for Baseline Static LTC of GFRP Joints                        | 94 |

## LIST OF FIGURES

|             |                                                                         |    |
|-------------|-------------------------------------------------------------------------|----|
| Figure 1.1  | Annual CO <sub>2</sub> emissions from fossil fuels                      | 2  |
| Figure 1.2  | EU CO <sub>2</sub> passenger car standards                              | 3  |
| Figure 1.3  | CO <sub>2</sub> emission from different sectors in US                   | 4  |
| Figure 1.4  | Materials used in Boeing 787                                            | 6  |
| Figure 1.5  | Factors affecting joint reliability                                     | 18 |
| Figure 2.1  | Urethane group form polyurethane resin                                  | 20 |
| Figure 2.2  | Vacuum bag illustration                                                 | 22 |
| Figure 2.3  | Autoclave minibonder                                                    | 22 |
| Figure 2.4  | Polycarbonate single lap joint illustration                             | 23 |
| Figure 2.5  | Autoclave profile illustration                                          | 25 |
| Figure 2.6  | Thermotron Environmental Chamber                                        | 26 |
| Figure 2.7  | Cyclic Temperature and Constant Humidity Profile                        | 27 |
| Figure 2.8  | Static LTC Test Setup with Polycarbonate Coupon                         | 27 |
| Figure 2.9  | Combined plot for load transfer capacity (LTC) of polycarbonate joints  | 29 |
| Figure 2.10 | Effect of cure temperature on baseline LTC of polycarbonate joints      | 30 |
| Figure 2.11 | Effect of cure pressure on baseline LTC of polycarbonate joints         | 31 |
| Figure 2.12 | Effect of temperature ramp rate on baseline LTC of polycarbonate joints | 31 |

## LIST OF FIGURES—Continued

|             |                                                                                                  |    |
|-------------|--------------------------------------------------------------------------------------------------|----|
| Figure 2.13 | Effect of cure time on baseline LTC of polycarbonate joints                                      | 32 |
| Figure 2.14 | Failure modes in bonded joints                                                                   | 35 |
| Figure 2.15 | Pure Shear Failure Mode in Polycarbonate Joints Bonded at Low Cure Temperature                   | 36 |
| Figure 2.16 | Pure Shear Failure Mode in Polycarbonate Joints Bonded at High Cure Temperature                  | 36 |
| Figure 2.17 | Normal Plot for Baseline Shear Strength of Polycarbonate Joints                                  | 39 |
| Figure 2.18 | Shear Strength of Baseline Polycarbonate Joints(a) Normal Plot of residuals (b) Residual vs. Run | 40 |
| Figure 2.19 | Single Variable Effect on Baseline Shear Strength for Polycarbonate Joints                       | 41 |
| Figure 3.1  | Reaction between bisphenol A and epichlorohydrin to form epoxy resin (prepolymer)                | 44 |
| Figure 3.2  | Cure Reaction of Epoxy Resin with Amine Hardener                                                 | 44 |
| Figure 3.3  | Cross-Linked Epoxy                                                                               | 45 |
| Figure 3.4  | Flow Diagram of The Stages of Thermoset Cure                                                     | 47 |
| Figure 3.5  | Time-Temperature transformation (TTT) Cure Diagram for Epoxy system                              | 49 |
| Figure 3.6  | DMA Sample Illustration                                                                          | 51 |
| Figure 3.7  | Autoclave Profile with Progress in Cure Illustration                                             | 52 |
| Figure 3.8  | Dynamic Mechanical Analyzer                                                                      | 53 |
| Figure 3.9  | DMA test setup                                                                                   | 54 |
| Figure 3.10 | DMA Result Illustration                                                                          | 54 |



## LIST OF FIGURES—Continued

|             |                                                                                                                    |    |
|-------------|--------------------------------------------------------------------------------------------------------------------|----|
| Figure 3.11 | DMA Results for Autoclave ID 1 for Three Samples                                                                   | 55 |
| Figure 3.12 | Cure Temp. ( $T_{\text{cure}}$ ) Vs. Glass Transition Temperature ( $T_g$ ) Graph For AF163-2K Epoxy Film Adhesive | 56 |
| Figure 3.13 | Glass Transition Temperature ( $T_g$ ) for all Autoclave process Combinations                                      | 58 |
| Figure 3.14 | Effect of Cure Temperature on Glass Transition Temperature ( $T_g$ ) of Epoxy Adhesive AF163-2K                    | 58 |
| Figure 3.15 | Effect of Cure Pressure on Glass Transition Temperature ( $T_g$ ) of Epoxy Adhesive AF163-2K                       | 59 |
| Figure 3.16 | Effect of Temperature Ramp Rate on Glass Transition Temperature ( $T_g$ ) of Epoxy Adhesive AF163-2K               | 60 |
| Figure 3.17 | Effect of Cure Time on Glass Transition Temperature ( $T_g$ ) of Epoxy Adhesive AF163-2K                           | 61 |
| Figure 3.18 | Cross-linking and Hydrogen Bonding in the Cured Epoxy                                                              | 62 |
| Figure 3.19 | FTIR Spectra for Epoxy Adhesive Cured at Different Curing Pressure                                                 | 63 |
| Figure 3.20 | Normal Plot for Glass Transition Temperature ( $T_g$ )                                                             | 64 |
| Figure 3.21 | Glass Transition Temperature (a) Normal Plot of residuals (b) Residual vs. Run                                     | 67 |
| Figure 3.22 | Single Variable Effect on Glass Transition Temperature ( $T_g$ )                                                   | 67 |
| Figure 4.1  | 3D Surface Roughness Inspection Image Data with $R_a = 370.51 \text{ Nm}$                                          | 69 |
| Figure 4.2  | Aluminum SLJ Illustration                                                                                          | 70 |
| Figure 4.3  | Static LTC Test Setup for Aluminum Joints                                                                          | 71 |
| Figure 4.4  | Combined plot for load transfer capacity (LTC) of Aluminum joints                                                  | 73 |

## LIST OF FIGURES—Continued

|             |                                                                                          |    |
|-------------|------------------------------------------------------------------------------------------|----|
| Figure 4.5  | Effect of Cure Temperature on Baseline LTC of AL-SLJ with Epoxy Adhesive AF163-2K        | 74 |
| Figure 4.6  | Effect of Cure Pressure on Baseline LTC of AL-SLJ with Epoxy Adhesive AF163-2K           | 75 |
| Figure 4.7  | Effect of Temperature Ramp rate on Baseline LTC of AL-SLJ with Epoxy Adhesive AF163-2K   | 76 |
| Figure 4.8  | Effect of Cure Time on Baseline LTC of AL-SLJ with Epoxy Adhesive AF163-2K               | 77 |
| Figure 4.9  | Failure modes in A1 SLJ's                                                                | 78 |
| Figure 4.10 | Normal Plot for Baseline Shear Strength of A1-SLJ's                                      | 80 |
| Figure 4.11 | Baseline Static LTC of A1-SLJ's (a) Normal Plot of Residuals (b) Residual vs Run         | 82 |
| Figure 4.12 | Single Variable Effect on baseline LTC of A1-SLJ's                                       | 82 |
| Figure 5.1  | Illustration of GFRP Joint with Epoxy AF163-2K adhesive                                  | 84 |
| Figure 5.2  | Static LTC Test Setup with GFRP SLJ                                                      | 86 |
| Figure 5.3  | Combined plot for load transfer capacity (LTC) of GFRP joints                            | 87 |
| Figure 5.4  | Effect of Cure Temperature on Baseline LTC of GFRP-SLJ with Epoxy Adhesive AF163-2K      | 88 |
| Figure 5.5  | Effect of Cure Pressure on Baseline LTC of GFRP-SLJ with Epoxy Adhesive AF163-2K         | 89 |
| Figure 5.6  | Effect of Temperature Ramp rate on Baseline LTC of GFRP-SLJ with Epoxy Adhesive AF163-2K | 90 |
| Figure 5.7  | Effect of Cure Time on Baseline LTC of GFRP-SLJ with Epoxy Adhesive AF163-2K             | 90 |
| Figure 5.8  | Effect of Environmental Loading on the LTC of GFRP Joints                                | 92 |

## LIST OF FIGURES—Continued

|             |                                                                                           |    |
|-------------|-------------------------------------------------------------------------------------------|----|
| Figure 5.9  | Failure modes in GFRP SLJ's                                                               | 92 |
| Figure 5.10 | Cohesive Failure Mode in GFRP Joints                                                      | 93 |
| Figure 5.11 | Normal Plot for Baseline Shear Strength of GFRP-SLJ's                                     | 95 |
| Figure 5.12 | Baseline Static LTC of GFRP-SLJ's (a) Normal Plot<br>Cohesive Failure Mode in GFRP Joints | 96 |
| Figure 5.13 | Single Variable Effect on baseline LTC of GFRP-SLJ's                                      | 97 |

## LIST OF ABBREVIATIONS

|      |                                |
|------|--------------------------------|
| SLJ  | Single Lap Joint               |
| LTC  | Load Transfer Capacity         |
| GFRP | Glass Fiber Reinforced Polymer |
| SEM  | Scanning Electron Microscopy   |
| Al   | Aluminum                       |
| Mg   | Magnesium                      |
| PC   | Polycarbonate                  |
| PU   | Polyurethane                   |
| VOC  | Volatile Organic Compound      |
| DMA  | Dynamic Mechanical Analyzer    |

# CHAPTER ONE

## INTRODUCTION AND LITERATURE SURVEY

### 1.1 General Overview

Recently the world is grappling with the challenges of climate change and limiting greenhouse gas (GHG) emissions including CO<sub>2</sub>, methane, and nitrous oxide. Industrial activities such as transportation, power plants, and energy-intensive industries produces CO<sub>2</sub> emissions which account for approximately 75% of greenhouse gas emissions [1], increasing global temperature by 1.5 °C, deemed relatively high. This phenomenon resulted in the United Nations Framework Convention on Climate Change being established in 1992. Later, in 1997, the Kyoto Protocol and the 2015 Paris Agreement were developed to combat global warming by limiting greenhouse gas emissions [2]. Figure 1.1 shows annual CO<sub>2</sub> emissions from fossil fuels, by world region.

In 2018, about a quarter of CO<sub>2</sub> emissions globally were from transportation (IEA, 2019), and projections from the International Transport Forum (ITF) suggest that in the absence of effective mitigation measures, global emissions from the transport sector will rise by another 60% by 2050 (ITF, 2019) [3-5]. The need to reduce carbon dioxide (CO<sub>2</sub>) emissions from the production of energy and other industrial activities has received increased global attention in recent years. At the end of 2013, the European Parliament and the Council of the European Union reached an agreement regarding two regulatory proposals that will implement mandatory 2020, CO<sub>2</sub> emission targets for new passenger cars and light-commercial vehicles in the European Union. The passenger car standards are 95 g/km of CO<sub>2</sub>, phasing in for 95% of vehicles in 2020 with 100% compliance in

2021. The light-commercial vehicle standards are 147 g/km of CO<sub>2</sub> for 2020. To achieve these goals, average CO<sub>2</sub> emissions from new cars will need to continue to fall rapidly [6-8]. Figure 1.2 provides a comparison of the EU CO<sub>2</sub> passenger car standards with similar regulations around the world.

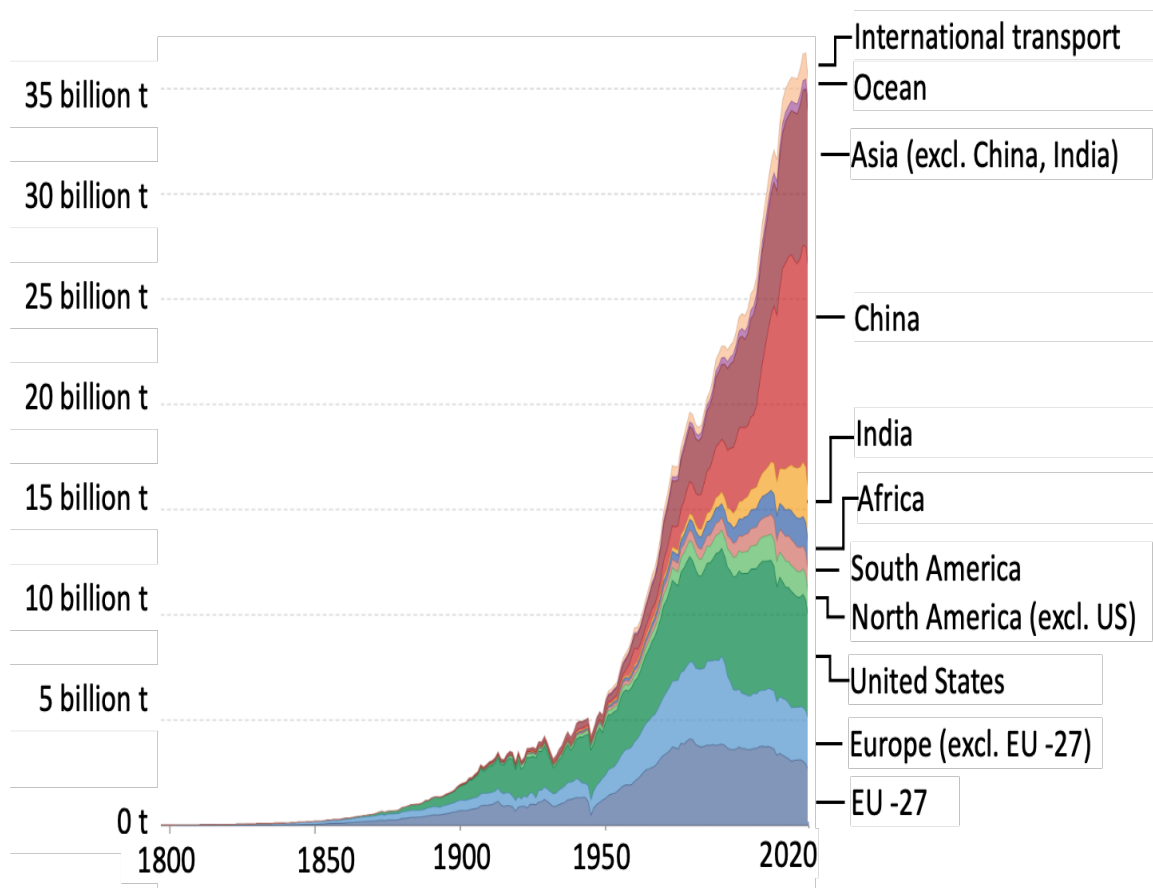


Figure 1.1 Annual CO<sub>2</sub> emissions from fossil fuels

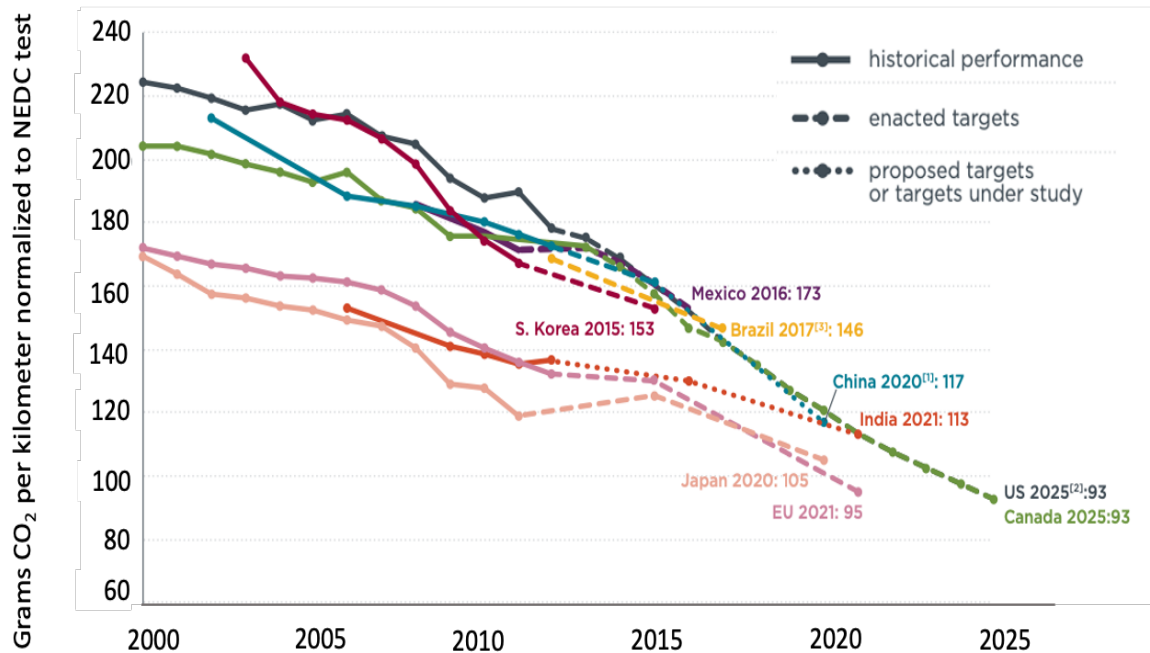


Figure 1.2 EU CO<sub>2</sub> passenger car standards

Figure 1.3 shows overview of the CO<sub>2</sub> emission from different sectors in US. The transportation sector is the largest direct source of GHG emissions, surpassing the power sector. Cars and light-duty trucks (including pickups and SUVs) are responsible for about 59% of transportation emissions. President Biden signed an executive order on Strengthening American Leadership in Clean Cars and Trucks, which sets target of making 50% transportation zero emission by 2030. In automotive industry, lightweight materials replacing the cast iron and traditional steel components offers great potential for increasing vehicle efficiency with reduced emission. A mid-size family car weight reduction of approximately 10% achieves a 6% improvement in fuel economy, along

with significant reduction in CO<sub>2</sub> emissions. Hence, deployment of lightweight materials in transportation and aerospace industry is essential key to carbon free economy.

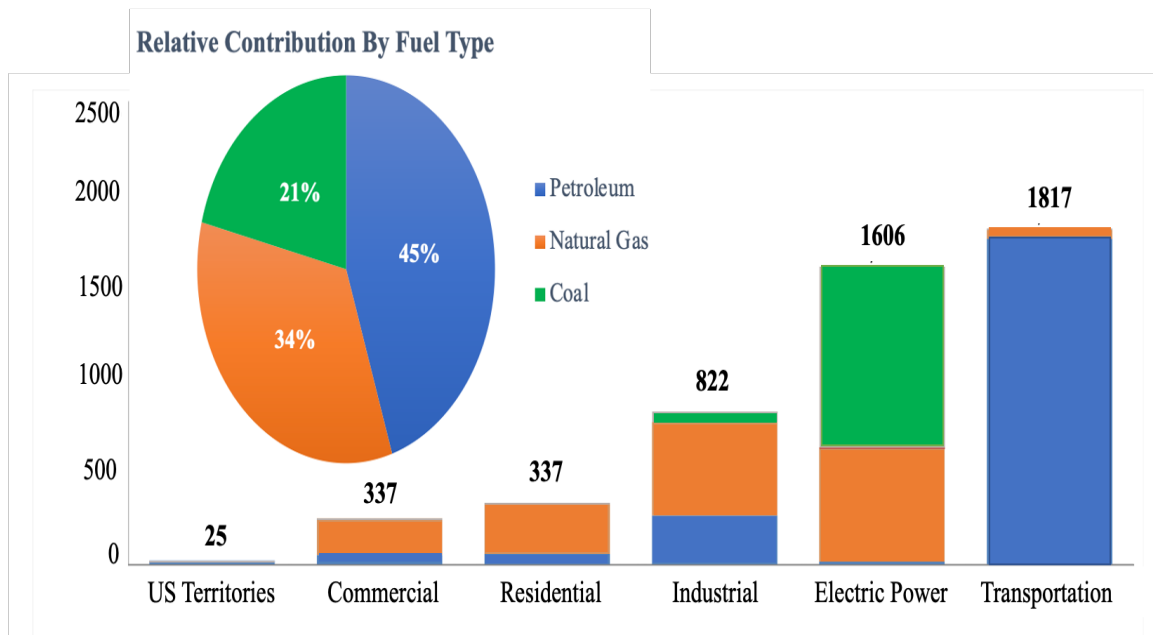


Figure 1.3 CO<sub>2</sub> emission from different sectors in US

## 1.2 Lightweight Solution

Rapid industrialization and urbanization are driving automotive industry to evolve and refines its product range and specifications to meet the ever-increasing customer requirements, economy, and green credentials. However, technological advancements also promote large amount of fuel consumption and a great challenge to the ecological balance. Thus, the application of light weight environment friendly materials (LWEFMs) in the automotive industry has seen a drastic growth in recent years. Industries such as



aerospace in addition other industries such as shipbuilding, railway, medical, nuclear, or agricultural also show increasing interest thanks to their inherent enthralling properties including low density, high stiffness, high corrosion resistance, good strength and fatigue performance, high specific strength, and dimensional stability. Reduced vehicle weight can be achieved either through structural light weight design or lightweight materials substitution [9]. Due to these reasons, one of the key focus areas of the automotive organizations has been shifted to manufacture these LWEFMs for body-in-white applications including aluminum alloy, magnesium alloy, high-strength steel, plastics, polymers, composites, and other alternative materials [10].

In this case, a car must be as durable and lightweight as possible [11,12]. This applying to reduce the weight of the vehicle reduces fuel consumption and CO<sub>2</sub> emissions without compromising performance [13-14]. Low-density materials are preferred for weight reduction in automobiles. Figure 1.4 gives the distribution of light weight material used in the Boeing 787. The Boeing 787 Dreamliner was a breakthrough commercial jet as it used light-weight composite carbon fiber material, rather than aluminum, to generate the best fuel efficiency in its class.

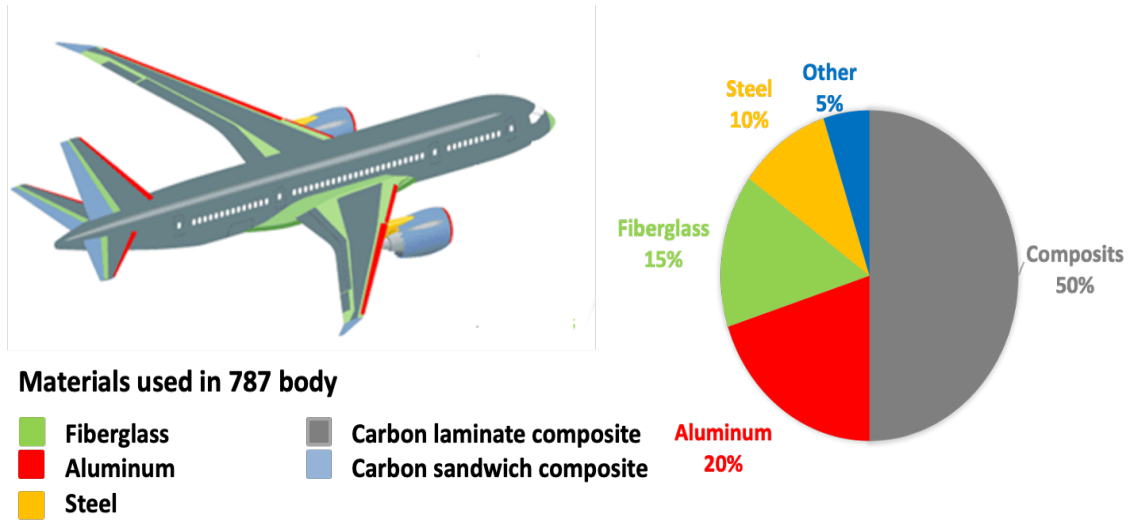


Figure 1.4 Materials used in Boeing 787

Table 1.1. Weight reduction by lightweight material

| Material                             | Weight Reduction (%) | Relative Cost (%) |
|--------------------------------------|----------------------|-------------------|
| Advanced high-strength steels (AHSS) | 15–25                | 100–150           |
| Glass fiber composites               | 25–35                | 100–150           |
| Aluminum                             | 40–50                | 130–200           |
| Magnesium                            | 55–60                | 150–250           |
| Carbon-fiber composites              | 55–60                | 200–1000          |

Mg and Al are two of the lightest metals and therefore offering a good choice for automobile production when weight is a critical design concept [15]. Compared to its competitor materials, Mg is 36% lighter than Al, 78% than steel. Also, Al is 65% lighter than steel [16] as shown in Table 1.1. As the use of these metals can greatly reduce the

weight of automobiles without sacrificing structural features. Therefore, up to 15% weight savings can be achieved with material substitution in automobiles [17]. The restrictions on energy demand and CO<sub>2</sub> emissions in vehicles are increasing the demand for the use of these lightweight materials [18]. Further increase in the use of light metals in auto- mobile production requires joint efforts from suppliers and auto- motive manufacturers. Although there has been work on the selection of lightweight materials for passenger cars, none of them considers the reduction of emissions from the fleet of passenger cars produced at the regional level. This is because it requires comprehensive analysis to assess the impact of the use of such materials on fuel and emission reduction and to determine its contribution to achieving specific emission targets [19]. Despite the difficulties, the researchers' suggestions on the subject encouraged our study by considering 20 years on the scale of automobile production in EU countries. The objective of the study is to focus on determining and discuss the effect of weight reduction on driving cycle exhaust CO<sub>2</sub> emissions in the European passenger car fleet due to the replacement of steel with Al and Mg-based on mathematical modeling.

### 1.3 Literature Survey

#### 1.3.1 Adhesive joints

One of the foremost challenges facing the aerospace, automotive industries is the need to decrease cost and increase fuel economy without sacrificing performance. Adhesive materials are perfectly suited to address these challenges. Adhesive joints are increasingly employed for bonding critical parts of industrial structures to permit construction of lightweight assemblages by replacing of conventional jointing elements

such as bolts, rivets, and weldments [20]. Therefore, adhesive joints become a key component in design, and their mechanical characterization is of utmost importance.

Additionally, adhesive joints should withstand long term of service conditions, including structural loads and exposure to hostile environments such as extreme temperature, water, and organic solvents, etc. [21]. Humid environments can be very severe, resulting in reversible or permanent changes to the adhesive (plasticization, swelling, hydrolysis) [22–24], and to the substrate/adhesive interface (corrosion, cracking, debonding, etc.) as described by Bowditch and others [25,26]. As a result, much work has been devoted to characterizing the strength of bonded joints. Moisture is absorbed by the adhesive in two different ways: as free water, which occupies the free spaces of the adhesive and is responsible for plasticization. Water is also absorbed as bound water, which forms single or multiple hydrogen bonds with the adhesive's polymer chain, resulting in swelling of the adhesive, plasticization and consequent decrease of strength and glass transition temperature ( $T_g$ ). Hu et al. [27] studied different adhesives in an extreme temperature environment and static performance of joint showed longer exposure leads to different failure modes. Da Silva et al. [28] studied effect of diffused moisture into the adhesive layer. Their results showed deterioration in bond strength after diffusion. Boubakri et al. [29] showed aging temperature and water are governing factors in the adhesive degradation.

Joint strength degradation due to long moisture exposure and then strength recovery after dehydration studied by A. Mubashar et al. [30]. Results showed loss of cohesive strength due to plasticization of the adhesive and primer was the main reason behind lowered performance of the joints. Sylvain Popineau et al [31] used 2H NMR and

gravimetric techniques, to explain water diffusion in an epoxy resin quantitatively by the Carter and Kibler theory based on Fickian approach. A dual stage uptake model for moisture absorption in the epoxy adhesive was proposed by W.K. Loh et al. [32] to explain increase in the saturation level with increasing relative humidity.

Strength of adhesively bonded structures depends on curing process parameters used during bonding. Nassar et al. [33] studied effect of cure temperature ( $T$ ), cure pressure ( $P$ ), temperature ramp rate ( $R_t$ ), pressure ramp rate ( $R_p$ ) and cure time ( $t$ ) on strength of polycarbonate joint at room temperature and after environmental loading. Their result established relation between bonding process variables and their interactions on the strength of polyurethane film adhesive.

### 1.3.2 Adhesive Characterization

The glass transition temperature ( $T_g$ ) is one of the most important parameters of an epoxy polymeric system.  $T_g$  determines the temperature boundary of significant changes in the enthalpic, viscoelastic, dilatometric etc. properties of all glass-forming materials. Several cure monitoring techniques like Differential scanning calorimetry (DSC), rheology, dynamic mechanical analysis (DMA), and thermal gravimetric analysis (TGA) are used to characterize the thermo-physical and mechanical properties of an epoxy during cure. DSC is primarily used to observe phase transitions including the melting point and the glass transition temperature ( $T_g$ ) as well as heat of reaction to measure degree of cure (DOC) before or after a cure cycle has been applied [34-36]. Another technique for material characterization is rheology which measures the viscosity,

shear storage modulus,  $G'$ , which is a measure of the sample's elastic properties, and shear loss modulus,  $G''$ , that is a measure of the sample's viscous properties [37,38]. Like rheology, DMA determines the viscoelastic properties of a material by applying a sinusoidal stress and measuring the strain in the material. DMA investigates the longitudinal moduli,  $E'$  and  $E''$ , and can be used to identify  $T_g$  as well as transitions associated with molecular motions [39,40].

Raykhere et al. [41] studied Dynamic shear strength of adhesive joints with aluminum and GFRP with four different epoxy and polyurethane adhesive. They reported that dynamic strength was always higher than the static strength for all adhesives; however, the amount of increase was different for different adhesives. Bellini et al. [42] investigated effect of operating temperature on aged single lap bonded joints on the mechanical strength of single lap bonded joints in CFRP and epoxy film (AF 163-2K) and paste (EA 9309 NA) adhesives subjected to different ageing conditions. Results showed joints made with the AF 163-2K, ageing did not particularly affect the apparent shear strength. While specimens made with the EA 9309NA, ageing has played a fundamental role in the apparent shear strength of the joints. Tests at 25 °C showed an increase in the strength of the joint aged in air, due to a post-cure effect of ageing on the adhesive; while in the case of joints aged in water the apparent resistance was directly proportional to the degradation of the adhesive.

F Kadioglu [43] investigated Effects of three different overlap lengths and two composite adherend thicknesses on the performance of adhesively bonded joints with AF 163-2K epoxy film under tensile and bending loadings. Tensile load tests showed

increase in the overlap length resulted in increase in the joint performance almost linearly.

Nathan Sharp et al. [44] utilized Molecular Dynamics Simulations to investigate effects of water on epoxy cure kinetics and glass transition temperature. Experimental tests showed that absorbed water in an uncured epoxy system caused an increase in cure rate at low degrees of cure and a decrease in cure rate at high degrees of cure. Molecular simulations indicated that the increase in cure rate was due to an increase in molecular self-diffusion of the epoxy molecules in the presence of water. Both experiments and simulations showed that water decreases  $T_g$ . Effects were small below 1% water by weight, but that  $T_g$  depression occurs much quickly with increasing water content above 1%.

M. D. Banea et al. [45] investigated effects of temperature and loading rate on the mechanical properties of a high temperature epoxy adhesive. Results showed increase in ductility (strain to failure) and reductions in ultimate strength were measured at elevated temperatures (100, 125 and 150°C). The Young's modulus decreased nonlinearly with the temperature. At room temperature and 100°C (below the  $T_g$ ), a reduced sensitivity of tensile strain to the test speed was found. At 150°C, the tensile failure strain increased linearly with the test speed, while at 125°C the ultimate tensile strain decreased at a higher test speed. The temperature effect on the properties of the adhesive was more significant than that of the strain rate. Kelly [46] studied quasi-static strength and fatigue life of hybrid (bonded/bolted) composite single-lap joints. Experimentation showed hybrid joining in combination with a stiff epoxy adhesive offered only limited improvements in structural performance.

Bartczak et al. [47] studied numerical analysis of Stress distribution in adhesively bonded joints and the loading capacity of hybrid joints for car steels. Results proved that the overlap size increase results in a smaller overlap rotation in relation to the loading force. The finite element program MSC was used to study the stress distribution.

B. Ellis et al. [48] used infrared spectroscopy to measure cure for the epoxy resin with amine hardener at 100°C and post cure time at 180°C. Density of epoxy increased with increase in temperature at low cure temperature reaching maximum. After that it decreased with extended cure time. G. Wisanrakkit et al. [49] developed continuous heating transformation (CHT) cure diagram for epoxy system at constant heating rates, with inclusion of events like gelation, vitrification, and devitrification. They also investigated use of glass transition temperature ( $T_g$ ) as a parameter to monitor the isothermal cure of a tetrafunctional aromatic diamine and a difunctional aromatic epoxy system to develop a theoretical model between  $T_g$  and degree of cure/ conversion ( $\alpha$ ) [50].

L. Banks and Bryan Ellis [51] studied different cured epoxy resins to determine glass transition temperature by using broad line proton NMR and stress-strain measurements. The glass transition temperatures ranged from 367 to 410 K and were found to be linearly related to the reciprocal of the number average molecular weight of the pre-polymer molecules.

Urbaniak [52] studied correlation between the glass transition temperature ( $T_g$ ) and the conversion degree ( $\alpha$ ) in the cure reaction of the epoxy system. Three model correlations of  $T_g = f(\alpha)$  developed from DiBenedetto equation by Pascault and Williams, by Oleinik and by Hale were verified. It was proved that the latter model best fits the



experimental results  $T_g$  versus an obtained with the differential scanning calorimetry (DSC) method. Bernath et al. [53] studied characterization and mathematical modeling of the reaction kinetics of a fast epoxy resin. The prediction accuracy of a simple (Kamal-Malkin) and a complex (Grindling) kinetic model was investigated and compared to each other for non-isothermal, isothermal, and cyclic temperature programs. The Grindling model was chosen because of its ability to account for premature vitrification.

Gracia-Fernández et al. [54] compared the glass transition temperature obtained from dynamic mechanical analysis (DMA) and temperature modulated differential scanning calorimetry (TMDSC). Observation showed frequency used in testing have measure impact on the  $T_g$  value. Hagen et al. [55] studied Comparison of Dynamic Mechanical Measurements and  $T_g$  Determinations using two different instruments. Tension test results showed differences in  $T_g$  values of approximately 10°C for epoxy adhesive, the higher temperature being associated with the DMTA instrument. O.V. Startsev et al. [56] compared different methods of thermal analysis (DSC, DMA, and TMA) to determine characteristic temperatures for epoxy polymers in the glass-transition range. Results showed a good agreement between all three methods.

Weller et al. [57] studied effect of the ambient conditions on the curing process of transparent epoxy adhesives, especially influence of reaction temperature on the curing speed, the thermo-mechanical properties and optical characteristics of the adhesives were studied. Kratz et al. [58] developed cure kinetics models for interleaf particle toughened epoxies using differential scanning calorimetry (DSC) tests to measure the heat flow of the system, and semi-empirical models were fitted to the data.

Courtois et al. [59] investigated a viscoelastic temperature and degree of cure dependent constitutive model for an epoxy resin. The model parameters were optimized by minimization of the differences between the model predictions and the experimental data, and the model predictions were successfully validated against an independent creep. Lange et al. [60] investigated transitions during isothermal cure of an epoxy-amine system. DMA (Dynamic mechanical analysis) confirmed gelation before vitrification. The magnitude of the vitrification transition expressed either as amount of change in heat capacity or as maximum value of loss tangent, was found to decrease approximately linearly with increasing cure temperature.

Puentes et al. [61] developed TTT (time–temperature-transformation) diagram for epoxy film adhesives using quasi-isothermal scans with initial fast ramps with differential scanning calorimetry (DSC). Non-isothermal and isothermal DSC scans were used to capture the reaction and the glass transition temperature. The glass transition temperature was modeled via DiBenedetto's equation. Fraga et al. [62] explored TTT cure diagram for an epoxy system consisting of a diglycidyl ether of bisphenol A and calcium carbonate. Gel times were measured as a function of temperature using two experimental methods: solubility test and dynamic mechanical analysis (DMA).

L. Banks and B. Ellis [63] studied correlation between absorbed water and the glass transition temperature of an epoxy resin. In the presence of 2.5 w/o absorbed water  $T_g$  is reduced to 378 K from 410 K. This large reduction of  $T_g$  by such a small amount of water was due to specific interactions. Segmental motion was increased because of the disruption of hydroxyl group hydrogen bonds by the absorbed water molecules.

G. Wisanrakkit and J. K. Gillham [64] explored glass transition temperature ( $T_g$ ) as a parameter to monitor the isothermal cure of a tetrafunctional aromatic diamine and a difunctional aromatic epoxy system. A one- to-one relationship between  $T_g$  and conversion that is independent of cure temperature was developed. Prior to vitrification the reaction was only kinetically controlled becomes diffusion controlled after vitrification.

A. Shokuhfar and B. Arab [65] used molecular dynamics (MD) was used to simulate the cross linking of diglycidyl ether of bisphenol-A (DGEBA) with diethylenetriamine (DETA) curing. The constant- strain (static) approach was used to calculate the mechanical properties of the uncured and cross-linked systems. They found good agreement between estimated material properties with experimental observations. Moreover, the improvements in the mechanical properties with increasing the cross-linking density was observed.

Moosburger-Will et al. [66] explored partial cross-linking degree of RTM6 epoxy resin. results showed significant dependence of glass transition temperature, density, and modulus on the curing history and the curing degree. Density and modulus decrease with increasing curing degree.

Y. Xu et al. [67] investigated effects of different curing pressures on the structure and properties of bisphenol A type epoxy adhesive film using DSC, Fourier transform infrared spectroscopy (FTIR), DMA, nano-indentation analysis, and tensile testing. Results showed increase in cure pressure from 0 MPa to 0.5 MPa FTIR have positive effect on formation of rigid carbonyl groups in the polymer and improvement in mechanical performance. Nano-indentation analysis showed that the elastic modulus of

the cured product increased significantly, from 2.92 GPa to 3.49 GPa. DMA results showed that the crosslinking densities of the cured epoxy films were improved by the increased curing pressure.

J. B. Enns et al. [68] studied the modulus, density, glass transition temperature ( $T_g$ ), and water absorption characteristics of an amine-cured resin DGEBA as a function of extent of cure. Results showed lower modulus and higher equilibrium moisture content of the more highly cured resins at room temperature were a consequence of the lower density which in turn is a result of the increase in  $T_g$  as a function of cure.

R. J. C. Carbas et al. [69] explored effect of curing temperature in the glass transition temperature,  $T_g$ , and stiffness of epoxy adhesives using DMA. Results showed when cured below the cure temperature,  $T_{cure}$ , at which the  $T_g$  of the fully cured network,  $T_{g\infty}$ , is achieved, the strength and stiffness of the adhesive increase as the cure temperature increases and the  $T_g$  is higher than the cure temperature. When cured above the  $T_{cure}$  at which the  $T_{g\infty}$  is achieved, the strength and stiffness decrease as the cure temperature increases and the  $T_g$  is higher than the cure temperature.

#### 1.4 Organization of Dissertation

Literature survey conducted showed most of the study is carried out on the different adhesive system and in service load or environmental load. Very few of them cover curing parameters of the adhesive joining process. The objective of the thesis is to investigate the curing process parameter interaction. The process parameters include Cure pressure, Pressure ramp rate, Cure temperature, Temperature ramp rate and cure time.

In this dissertation, the contents are organized by the adherend used to single lap joint (SLJ); namely, polycarbonate, Aluminum and glass reinforced fiber plastics

(GRP). One chapter is dedicated to the epoxy film adhesive characterization. Static performance is investigated for lightweight similar joints under various environmental conditions. Structural adhesives are used to investigate mechanical performance as well as failure. Figure 1.5 shows flow different factors affecting joint reliability considered in dissertational research.

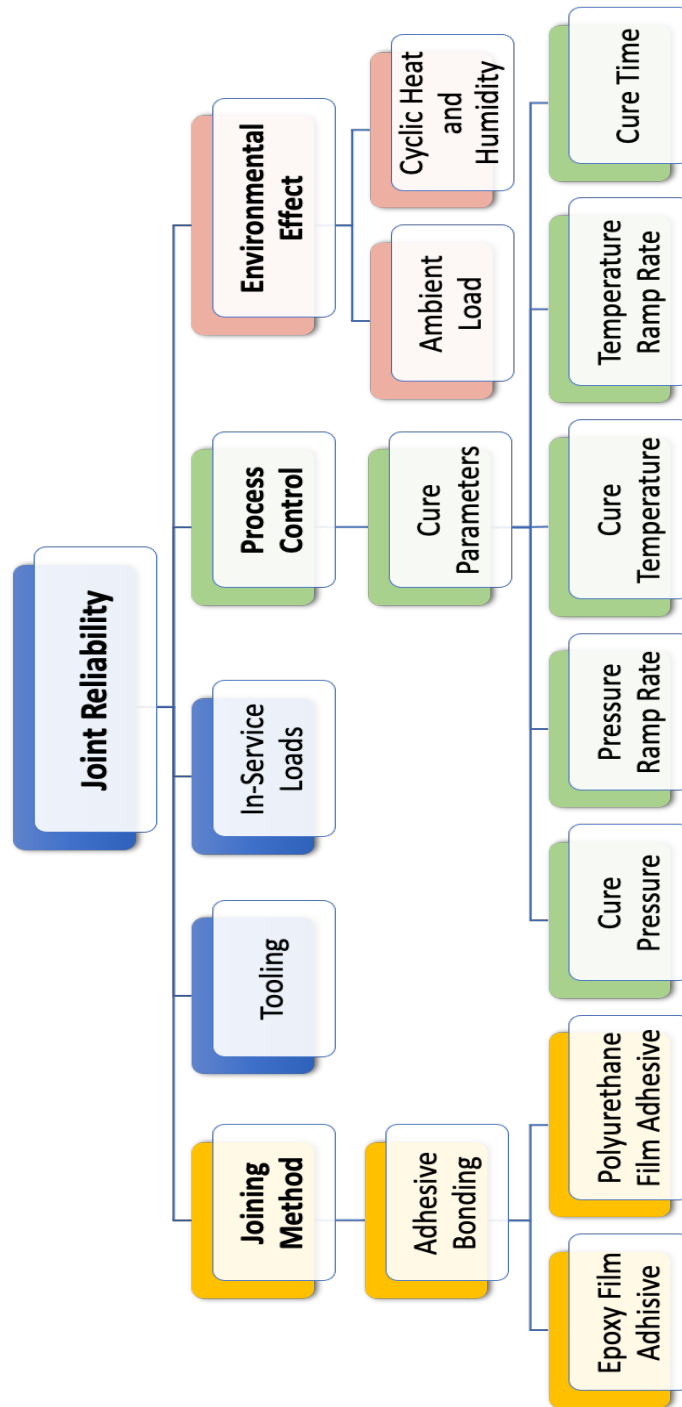


Figure 1.5 Factors Affecting Joint Reliability

## CHAPTER TWO

### POLYCARBONATE BONDED JOINT WITH POLYURETHANE ADHESIVE

#### 2.1 Introduction

Over the past few decades, the demand for polycarbonate as a major engineering plastic has increased because due to characteristic properties: toughness, transparency, self-extinguishing characteristic, and heat resistance. These desirable properties, combined with superior dimensional stability and good electrical resistance, have led to wide applications in automobile parts, electrical parts, optical materials, and steam sterilizable medical equipment. This section provides an experimental study of the effect of environmental loads on the static load transfer capacity of bonded single lap joints of polycarbonate.

#### 2.2 Materials

Lightweight material polycarbonate lexan was used. Single lap joints are bonded using polyurethane film adhesive. Figure 2.1 depicts the basic chemistry of polyurethane film adhesive. The soft block, built out of a polyol and an isocyanate, is responsible for the flexibility and elastomeric characteristic while the hard block, constructed from a chain extender and isocyanate, gives a polyurethane its toughness and physical performance properties. Surface of adherend was cleaned using compressed air to remove dirt particles. Their material properties of adherend and adhesives are shown in Table 2.1 and 2.2.

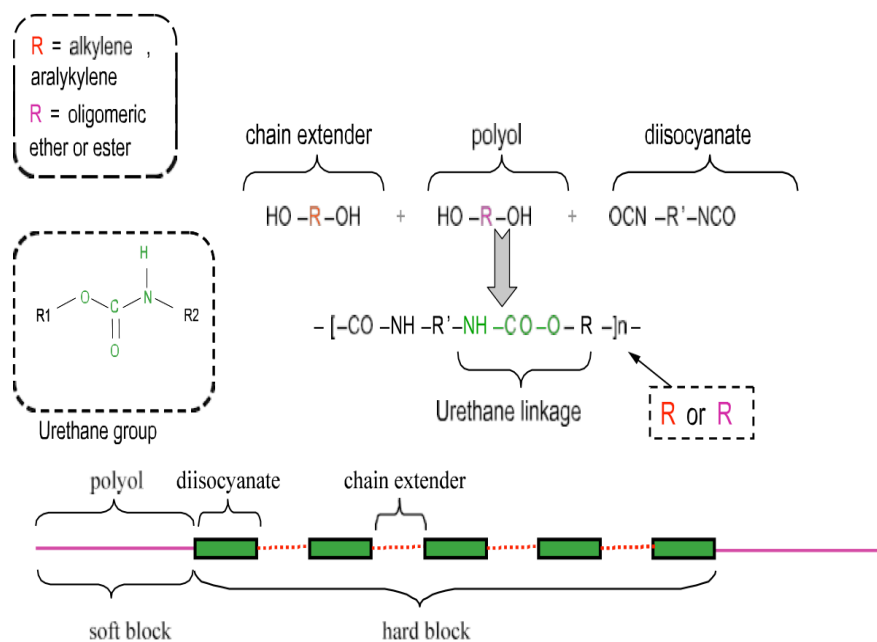


Figure 2.1 Urethane group form polyurethane resin

Table 2.1 Polycarbonate Adherend Mechanical Properties

| Property                  | Unit     | Value |
|---------------------------|----------|-------|
| Tensile Yield Strength    | MPa      | 62    |
| Tensile Ultimate Strength | MPa      | 65.5  |
| Shear Yield Strength      | MPa      | 41    |
| Shear Ultimate Strength   | MPa      | 69    |
| Young's Modulus           | GPa      | 2.6   |
| Hardness                  | Rockwell | M70   |
| Poisson's Ratio           |          | 0.37  |



### 2.3 Joining Procedure

Polycarbonate adherends are bonded together using polyurethane film adhesive PE399 using autoclave minibonder. Adhesive is an aliphatic polyether thermoplastic polyurethane film manufactured by Huntsman

Table 2.2 Polyurethane Adhesive Mechanical Properties

| Property                     | Unit    | Value |
|------------------------------|---------|-------|
| Tensile Strength             | MPa     | 45    |
| Elongation @ break           | %       | 500   |
| 100% Modulus                 | MPa     | 2     |
| Specific Gravity             |         | 1.07  |
| Hardness                     | Shore A | 80    |
| Glass Transition Temperature | °C      | -36   |

Polyurethane film adhesive is cut in the 1” X 1” pieces and placed in between two polycarbonate adherends. This loosely assembled joint was placed in vacuum bag with support plate to avoid bending of coupon during curing process as shown in Figure 2.2. The vacuum bag was transferred into autoclave to begin lamination process as shown in Figure 2.3. The single pal joint (SLJ) is illustrated in the Figure 2.4. The autoclave curing process profile and manufacturer recommended curing parameters are shown in Figure 2.5 Table 2.3, respectively.

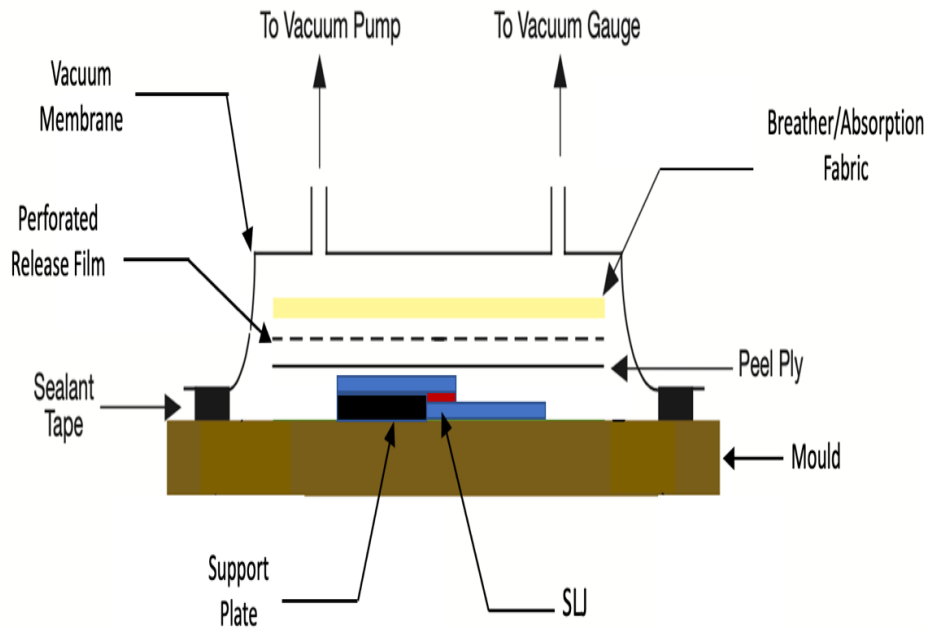


Figure 2.2 Vacuum Bag Illustration

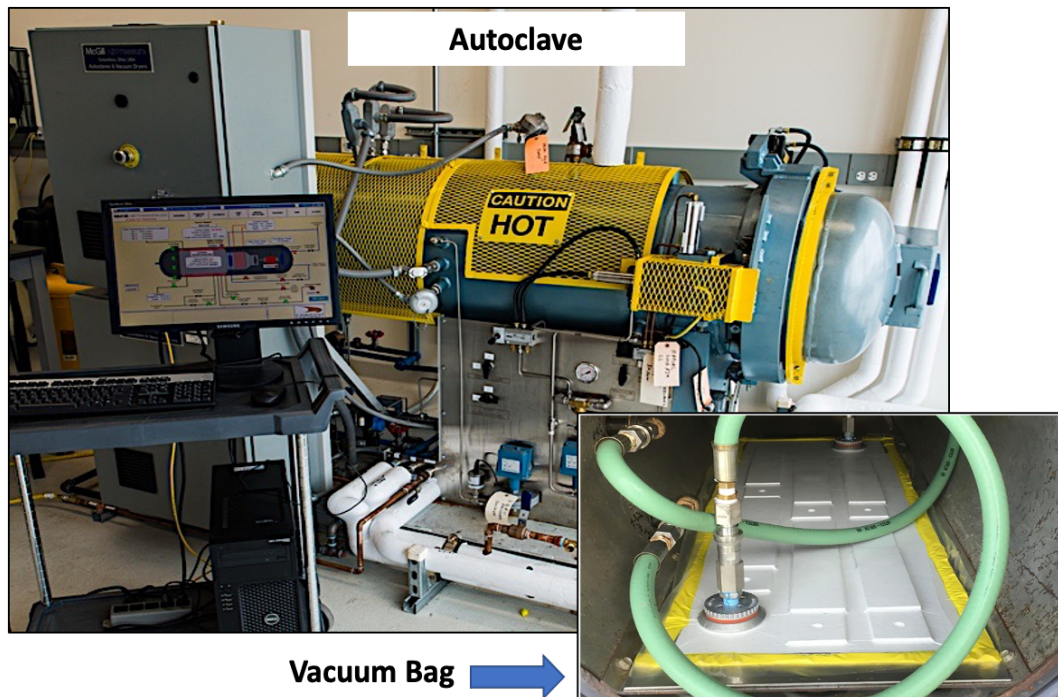


Figure 2.3 Autoclave Minibonder

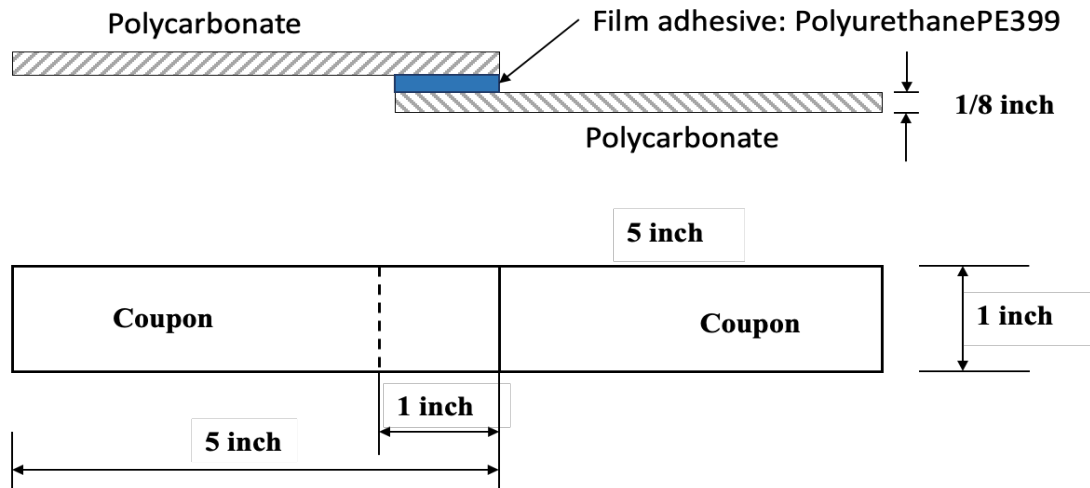


Figure 2.4 Polycarbonate Single Lap Joint Illustration

Table 2.3 Autoclave Bonding Process Variable Level

| Autoclave Bonding Process Variable                      | Two Levels of Autoclave Process Variables |               |
|---------------------------------------------------------|-------------------------------------------|---------------|
|                                                         | Minimum                                   | Maximum       |
| Cure Pressure [Psi]                                     | $P_1 = 50$                                | $P_2 = 100$   |
| Cure Temperature [ $^{\circ}\text{F}$ ]                 | $T_1 = 200$                               | $T_2 = 260$   |
| Temperature ramp rate [ $^{\circ}\text{F}/\text{min}$ ] | $R_{t1} = 2$                              | $R_{t2} = 7$  |
| Pressure ramp rate [Psi/min]                            | $R_{p1} = 10$                             | $R_{p2} = 15$ |
| Cure time [minute]                                      | $t_1 = 40$                                | $t_2 = 100$   |

Table 2.4 Autoclave Bonding Process Combinations

| <b>Process<br/>Combination ID</b> | <b>Cure Process<br/>Variables</b>                                                    | <b>Process<br/>Combination ID</b> | <b>Cure Process<br/>Variables</b>                                                    |
|-----------------------------------|--------------------------------------------------------------------------------------|-----------------------------------|--------------------------------------------------------------------------------------|
| 1                                 | T <sub>1</sub> , P <sub>1</sub> , R <sub>t1</sub> , R <sub>p1</sub> , t <sub>1</sub> | 17                                | T <sub>1</sub> , P <sub>1</sub> , R <sub>t1</sub> , R <sub>p1</sub> , t <sub>2</sub> |
| 2                                 | T <sub>1</sub> , P <sub>2</sub> , R <sub>t1</sub> , R <sub>p1</sub> , t <sub>1</sub> | 18                                | T <sub>1</sub> , P <sub>2</sub> , R <sub>t1</sub> , R <sub>p1</sub> , t <sub>2</sub> |
| 3                                 | T <sub>1</sub> , P <sub>1</sub> , R <sub>t1</sub> , R <sub>p2</sub> , t <sub>1</sub> | 19                                | T <sub>1</sub> , P <sub>1</sub> , R <sub>t1</sub> , R <sub>p2</sub> , t <sub>2</sub> |
| 4                                 | T <sub>1</sub> , P <sub>2</sub> , R <sub>t1</sub> , R <sub>p2</sub> , t <sub>1</sub> | 20                                | T <sub>1</sub> , P <sub>2</sub> , R <sub>t1</sub> , R <sub>p2</sub> , t <sub>2</sub> |
| 5                                 | T <sub>2</sub> , P <sub>1</sub> , R <sub>t1</sub> , R <sub>p1</sub> , t <sub>1</sub> | 21                                | T <sub>2</sub> , P <sub>1</sub> , R <sub>t1</sub> , R <sub>p1</sub> , t <sub>2</sub> |
| 6                                 | T <sub>2</sub> , P <sub>2</sub> , R <sub>t1</sub> , R <sub>p1</sub> , t <sub>1</sub> | 22                                | T <sub>2</sub> , P <sub>2</sub> , R <sub>t1</sub> , R <sub>p1</sub> , t <sub>2</sub> |
| 7                                 | T <sub>2</sub> , P <sub>1</sub> , R <sub>t1</sub> , R <sub>p2</sub> , t <sub>1</sub> | 23                                | T <sub>2</sub> , P <sub>1</sub> , R <sub>t1</sub> , R <sub>p2</sub> , t <sub>2</sub> |
| 8                                 | T <sub>2</sub> , P <sub>2</sub> , R <sub>t1</sub> , R <sub>p2</sub> , t <sub>1</sub> | 24                                | T <sub>2</sub> , P <sub>2</sub> , R <sub>t1</sub> , R <sub>p2</sub> , t <sub>2</sub> |
| 9                                 | T <sub>1</sub> , P <sub>1</sub> , R <sub>t2</sub> , R <sub>p1</sub> , t <sub>1</sub> | 25                                | T <sub>1</sub> , P <sub>1</sub> , R <sub>t2</sub> , R <sub>p1</sub> , t <sub>2</sub> |
| 10                                | T <sub>1</sub> , P <sub>2</sub> , R <sub>t2</sub> , R <sub>p1</sub> , t <sub>1</sub> | 26                                | T <sub>1</sub> , P <sub>2</sub> , R <sub>t2</sub> , R <sub>p1</sub> , t <sub>2</sub> |
| 11                                | T <sub>1</sub> , P <sub>1</sub> , R <sub>t2</sub> , R <sub>p2</sub> , t <sub>1</sub> | 27                                | T <sub>1</sub> , P <sub>1</sub> , R <sub>t2</sub> , R <sub>p2</sub> , t <sub>2</sub> |
| 12                                | T <sub>1</sub> , P <sub>2</sub> , R <sub>t2</sub> , R <sub>p2</sub> , t <sub>1</sub> | 28                                | T <sub>1</sub> , P <sub>2</sub> , R <sub>t2</sub> , R <sub>p2</sub> , t <sub>2</sub> |
| 13                                | T <sub>2</sub> , P <sub>1</sub> , R <sub>t2</sub> , R <sub>p1</sub> , t <sub>1</sub> | 29                                | T <sub>2</sub> , P <sub>1</sub> , R <sub>t2</sub> , R <sub>p1</sub> , t <sub>2</sub> |
| 14                                | T <sub>2</sub> , P <sub>2</sub> , R <sub>t2</sub> , R <sub>p1</sub> , t <sub>1</sub> | 30                                | T <sub>2</sub> , P <sub>2</sub> , R <sub>t2</sub> , R <sub>p1</sub> , t <sub>2</sub> |
| 15                                | T <sub>2</sub> , P <sub>1</sub> , R <sub>t2</sub> , R <sub>p2</sub> , t <sub>1</sub> | 31                                | T <sub>2</sub> , P <sub>1</sub> , R <sub>t2</sub> , R <sub>p2</sub> , t <sub>2</sub> |
| 16                                | T <sub>2</sub> , P <sub>2</sub> , R <sub>t2</sub> , R <sub>p2</sub> , t <sub>1</sub> | 32                                | T <sub>2</sub> , P <sub>2</sub> , R <sub>t2</sub> , R <sub>p2</sub> , t <sub>2</sub> |

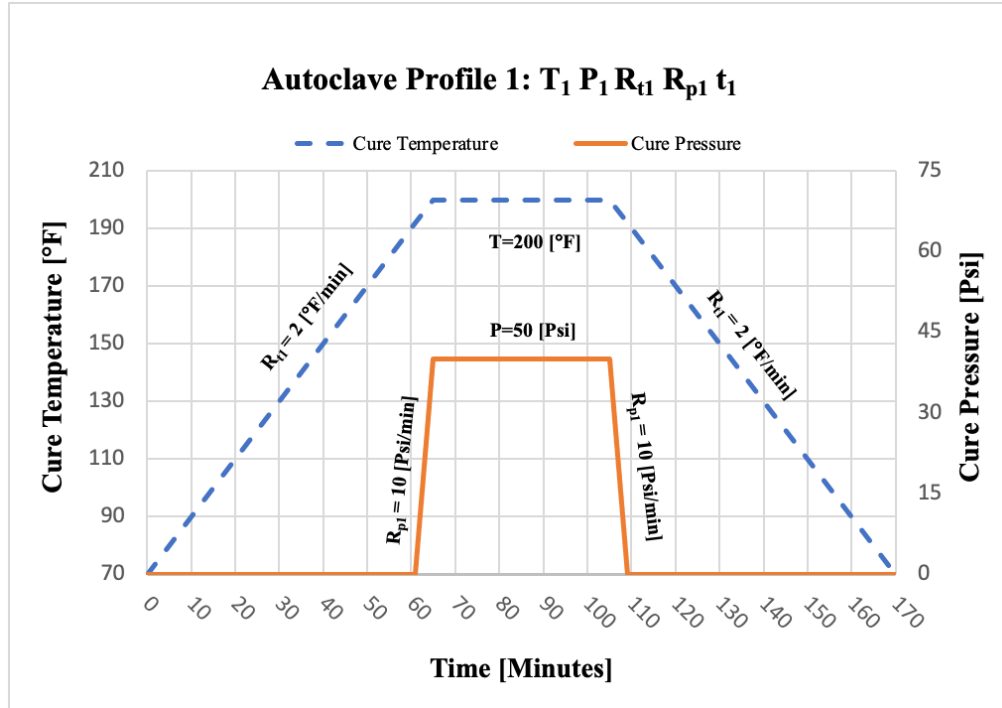


Figure 2.5 Autoclave Profile Illustration

## 2.4 Experimental Procedure and Test Setup

Polycarbonate test coupons from 32 different combinations of autoclave processes variables were tested in tensile shear for load transfer capacity (LTC) at ambient conditions to establish baseline results. Afterwards, the effect of environmental load was investigated with cyclic heat and high relative humidity conditions for using thermotron environmental chamber as shown in Figure 2.6. Six test coupons were autoclave bonded for each 32- autoclave bonding process. From which three polycarbonate coupons were tested for baseline LTC at ambient conditions. Other set of three polycarbonate SLJ's were subjected to 12-hrs, six cycles of heat at high relative humidity (RH) of 85% as shown in Figure 2.7. Average test data is reported.

Static LTC of polycarbonate coupons was evaluated using MTS 810 Material Testing System, shown in Figure 2.8. Coupons were held inside specially designed fixture and gripped vertically on MTS system. A quasi-static axial load is applied to the coupon at a constant speed of 1.27 mm/min. Displacement and forces are recorded by MTS data acquisition system. Failure modes have been documented for all test coupons.



Figure 2.6 Thermotron Environmental Chamber

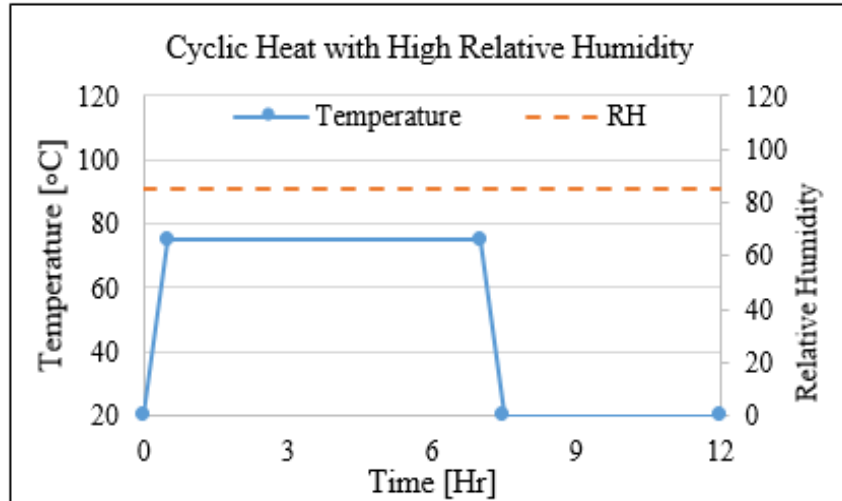


Figure 2.7 Cyclic Temperature and Constant Humidity Profile



Figure 2.8 Static LTC Test Setup with Polycarbonate Coupon

#### 2.4.1 Baseline Static Load Transfer Capacity (LTC)

In this section experimental results are presented and discussed. Figure 2.8 gives comparative overview of static performance of 32 autoclave processes designed with all possible combination of five process variables. Baseline static LTC is higher for all autoclave process when compared to static LTC after cyclic heat at high relative humidity. Higher baseline static LTC of 4037.2 N was observed autoclave process variables of cure temperature  $T_2 = 260$  °F, cure pressure  $P_1 = 50$  Psi, temperature ramp rate  $R_{t1} = 2$  °F /min, pressure ramp rate  $R_{p1} = 10$  Psi/min, cure time  $t_2 = 100$  min. Lower baseline static LTC 2020.3 N was observed autoclave process variables of cure temperature  $T_1 = 200$  °F, cure pressure  $P_2 = 100$  Psi, temperature ramp rate  $R_{t2} = 7$  °F /min, pressure ramp rate  $R_{p1} = 10$  Psi/min, cure time  $t_1 = 40$  min. Baseline static LTC reduced after cyclic heat at high relative. Higher percentage reduction in LTC observed for autoclave processes with low cure temperature than high cure temperature. Highest reduction of 49% observed for autoclave process ID 10 with cure temperature  $T_1 = 200$  °F, cure pressure  $P_2 = 100$  Psi, temperature ramp rate  $R_{t2} = 7$  °F /min, pressure ramp rate  $R_{p1} = 10$  Psi/min, cure time  $t_1 = 40$  min. Lowest LTC reduction of 11% observed for autoclave process ID 30 with cure temperature  $T_2 = 260$  °F, cure pressure  $P_2 = 100$  Psi, temperature ramp rate  $R_{t2} = 7$  °F /min, pressure ramp rate  $R_{p1} = 10$  Psi/min, cure time  $t_2 = 100$  min.

Autoclave process with low cure temperature  $T_1$  in combination with the high cure pressure  $P_2$  (Autoclave Process ID – 2, 4, 10) have lower LTC as compared to the combination of low cure temperature  $T_1$  and low cure pressure  $P_1$  (Autoclave Process ID – 1, 3, 9).



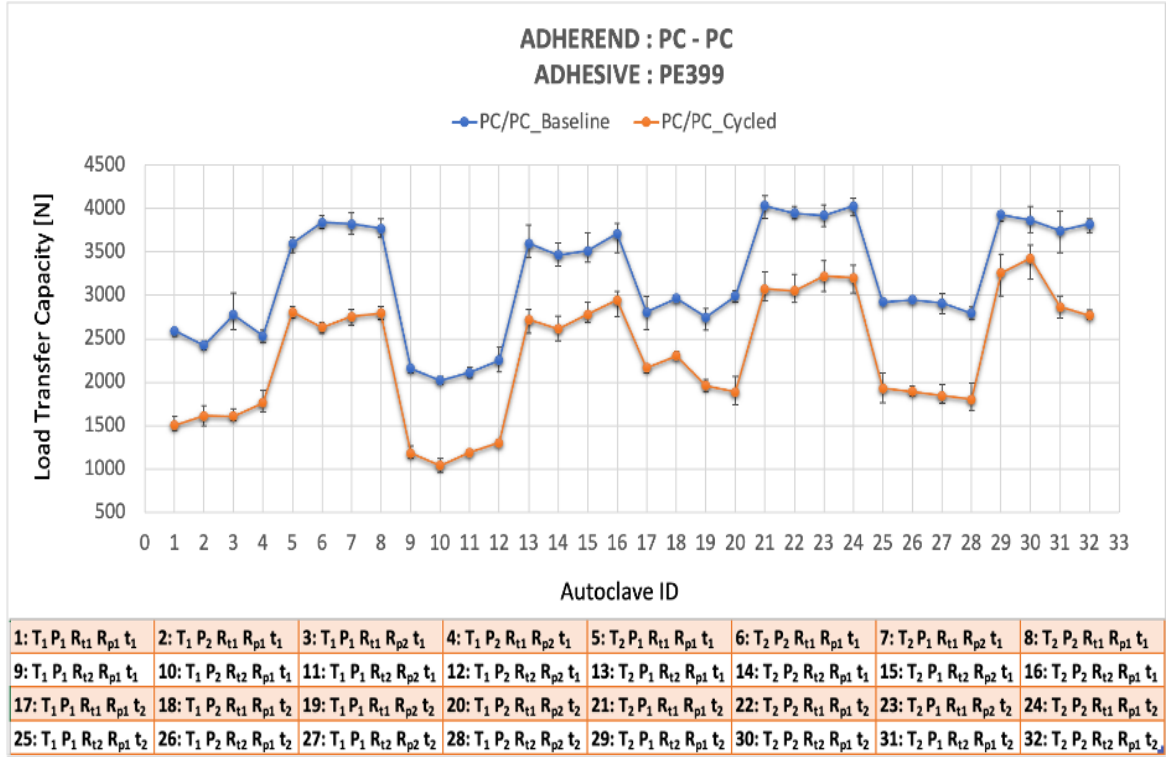


Figure 2.9 Combined Plot for Load Transfer Capacity (LTC) of Polycarbonate Joints

Polycarbonate SLJ bonded with process variables cure temperature  $T_2 = 260^\circ\text{F}$ , cure pressure  $P_2 = 100$  Psi,  $t_2 = 100$  min have negative effect on the LTC.

Figure 2.9 shows baseline static performance of polycarbonate coupons is higher for high cure temperature ( $T_2 = 260^\circ\text{F}$ ) when compared to low cure temperature ( $T_1 = 200^\circ\text{F}$ ) for all autoclave processes when other variables ( $P$ ,  $R_t$ ,  $R_p$ ,  $t$ ) remained same. Average static LTC for coupons bonded at high cure temperature is 3790 N, while those bonded at low cure temperature has 2622 N average LTC. Higher increase in LTC was observed for autoclave processes with cure pressure  $P_2 = 100$  Psi, temperature ramp rate

$R_{t2} = 7\text{ }^{\circ}\text{F}/\text{min}$ , pressure ramp rate  $R_{p2} = 15\text{ Psi}/\text{min}$ , cure time  $t_1 = 40\text{ min}$ , where LTC increased from 2809 N at low cure temperature to 3713 N at high cure temperature.

Figure 2.10 shows effect of cure pressure on baseline static LTC at room conditions when other process variables remained same ( $T$ ,  $R_t$ ,  $R_p$ ,  $t$ ). Average LTC for low cure pressure and high cure pressure was 3200 N and 3212 N. It is observed that effect of cure pressure alone on LTC is insignificant.

Figure 2.11 shows effect of temperature ramp rate on static LTC when other process variables remained same ( $T$ ,  $P$ ,  $R_p$ ,  $t$ ). It is observed that high temperature ramp rate has negative impact on LTC. Average LTC for low temperature ramp rate and high temperature ramp rate was 3252 N and 3110 N respectively.

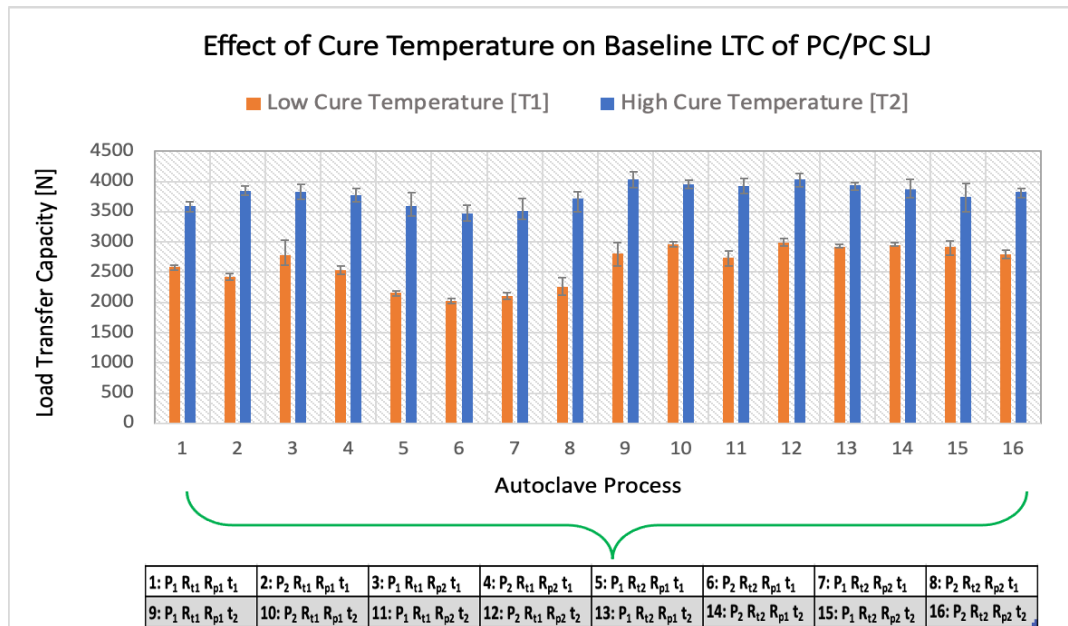


Figure 2.10 Effect of Cure Temperature on Baseline LTC of Polycarbonate Joints

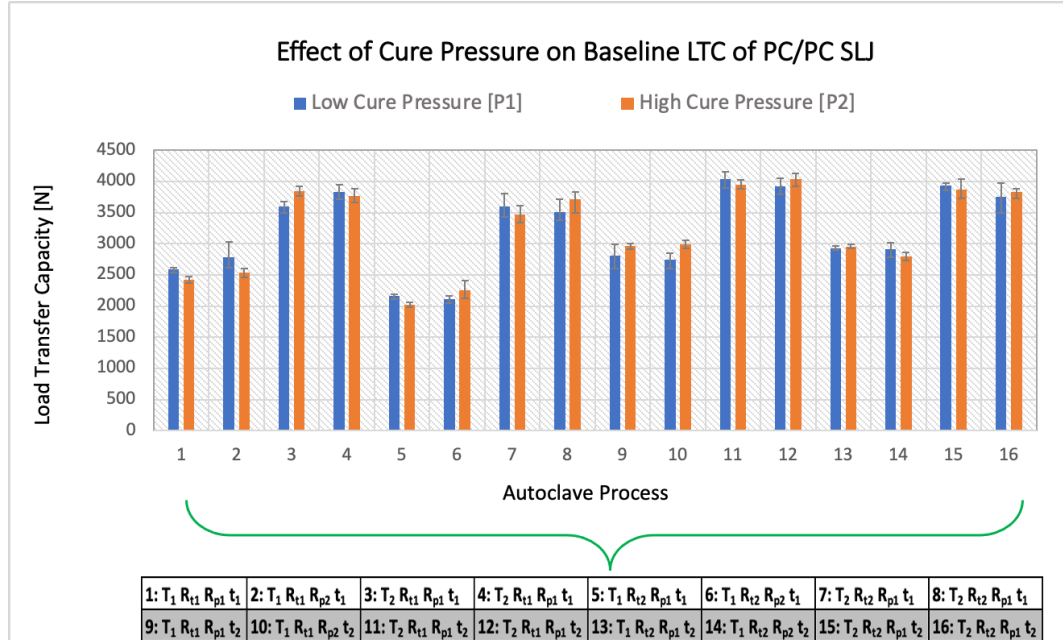


Figure 2.11 Effect of Cure Pressure on Baseline LTC of Polycarbonate Joint

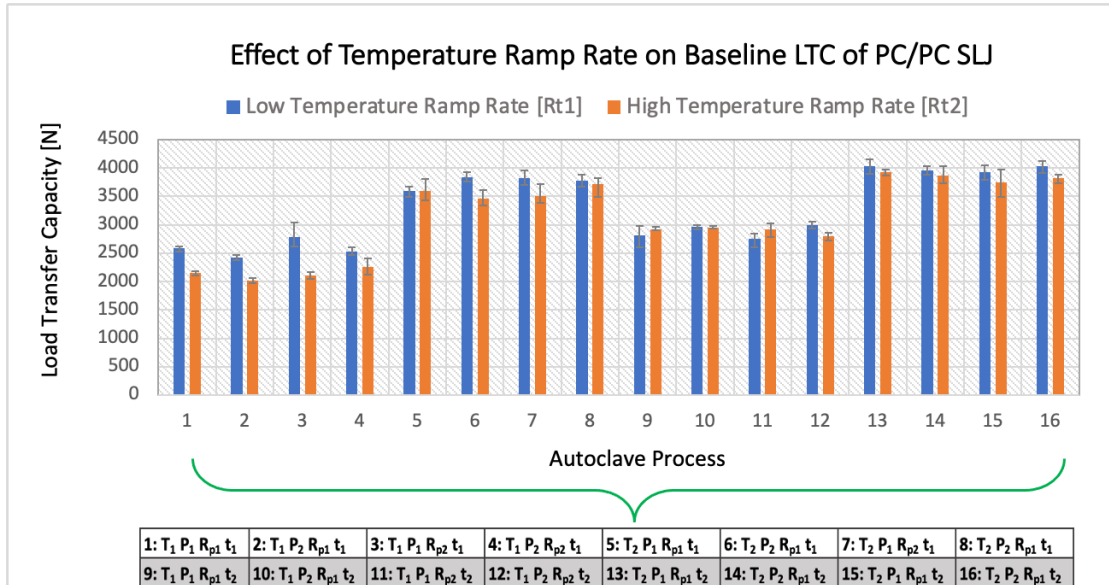


Figure 2.12 Effect of Temperature Ramp Rate on Baseline LTC of Polycarbonate Joint

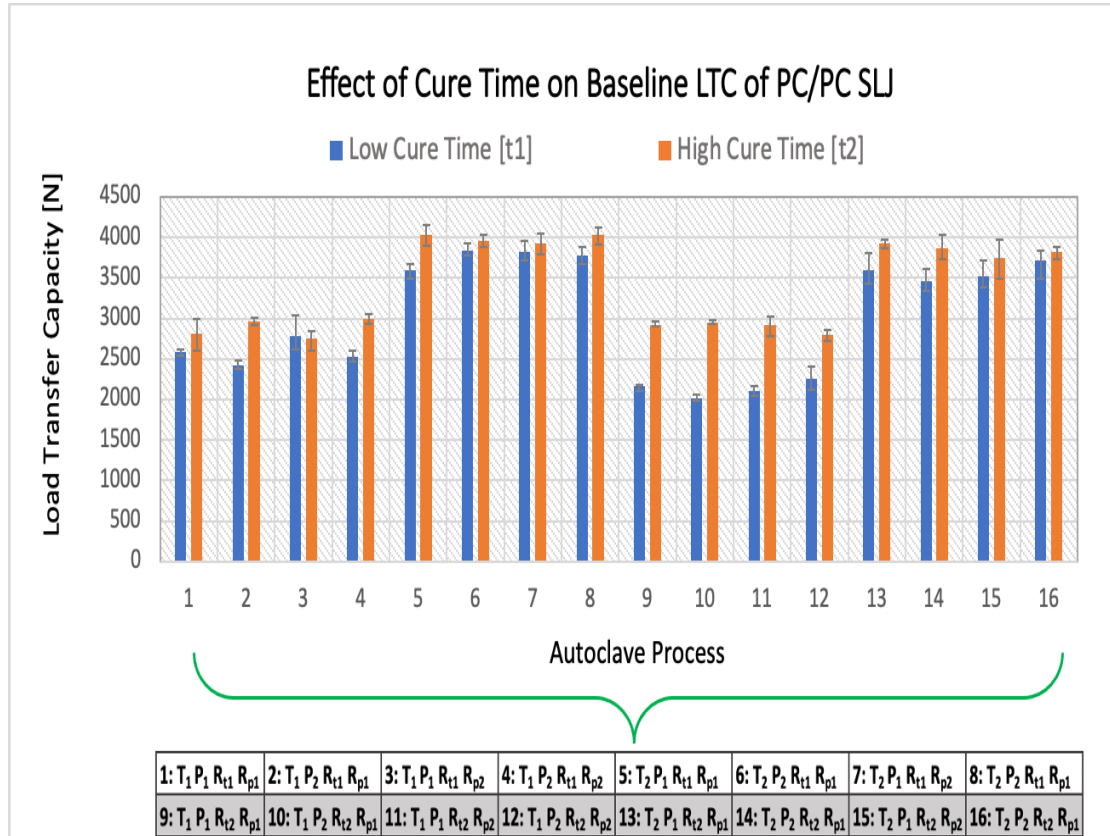


Figure 2.13 Effect of Cure Time on Baseline LTC of Polycarbonate Joint

Figure 2.12 shows effect of cure time on baseline static LTC, when other process variables remained same ( $P$ ,  $T$ ,  $R_t$ ,  $R_p$ ). It is observed that for most of autoclave processes, high soak time ( $t_2 = 100$  min) improved static performance of polycarbonate coupons. Average static LTC for low cure time and high cure time was 3012 N and 3400 N.

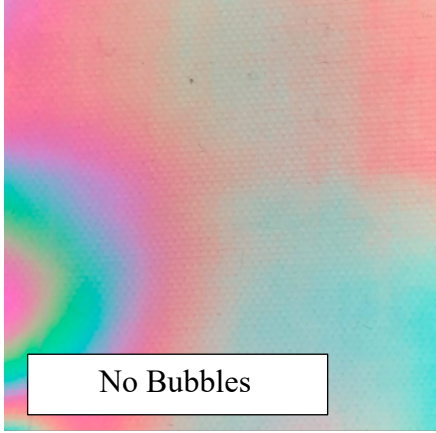
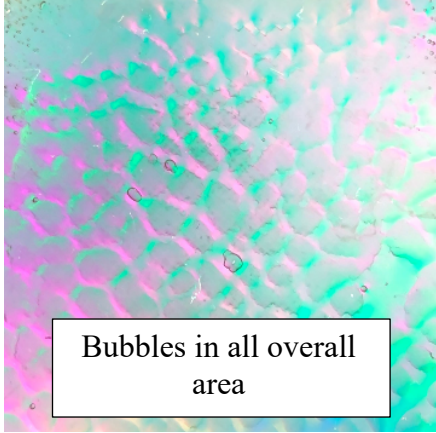
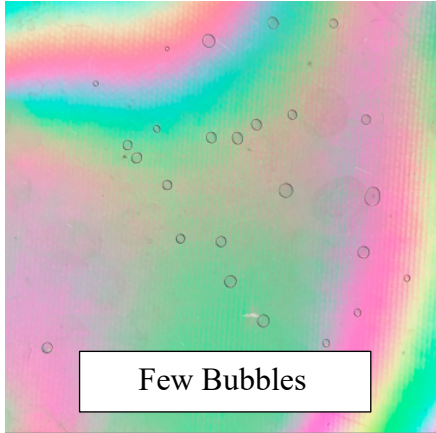
#### 2.4.2 Environmental Cycling

From the visual inspection of polycarbonate coupons, it is observed that cure temperature ( $T$ ) is most significant factor in the diffusion of moisture inside adhesive

layer. Table 2.4 presents visual appearance of polycarbonate coupon joint bonded at low/high cure temperature at ambient conditions and after environmental loading. Coupons that autoclave bonded with low cure temperature ( $T_1$ ) showed presence of more bubble inside adhesive layer after heat cycling at high relative humidity of 85% when compared to those bonded at high cure temperature ( $T_2$ ). Low cure temperature ( $T_1$ ) in combination with low cure time ( $t_1$ ) (Autoclave ID 1-4 ,9-12) were more susceptible to moisture diffusion than its combination with high cure time ( $t_2$ ) (Autoclave ID 17-20 ,25-28). Whereas High cure temperature, high cure time ( $t_2$ ) in combination with low pressure ramp rate ( $R_{p1}$ ) (Autoclave ID 21,22,29,30) have better resistance to moisture diffusion when compared to their combination with high pressure ramp rate ( $R_{p2}$ ) (Autoclave ID 23,24,31,32).

Figure 2.13 shows the failure modes in the adhesively bonded joint under tensile loading. All coupons tested in shear at ambient conditions failed with peel starting at edge progressed towards middle of joint and when load carrying area reduced to minimal, coupon failed in shear (Figure 2.15). Similar failure mode was observed for coupon with moderate bubble inclusion which were bonded at high cure temperature ( $T_2$ ). Diffusion of relative high moisture in adhesive layer for coupons bonded at low cure temperature ( $T_1$ ) showed changed failure mode from peel and shear to pure shear (Figure 2.14). Goglio L. and Rezaei M. [14] had similar findings after degradation of Epoxy-Steel single lap joints immersed in water. Their results showed formation of blisters created damage mechanism and changed failure mode.

Table 2.5 Joint Visual Inspection for Two Level of Cure Temperature Bonded Coupons

|                       | Baseline                                                                                             | Cyclic Heat at 85% RH                                                                                                 |
|-----------------------|------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------|
| Low Cure Temperature  |  <p>No Bubbles</p>  |  <p>Bubbles in all overall area</p> |
| High Cure Temperature |  <p>No Bubbles</p> |  <p>Few Bubbles</p>                |

A failure mode characteristic of a bonded SLJ without environmental effect was different from all others as polycarbonate adherend began to fail before a joint did. This phenomenon explains that adhesion strength between two adherends overcome the tensile yield strength of polycarbonate material. The polycarbonate adherend started to stretch after reaching its yield point during LTC testing, and bonded area was at 4.5 degrees of

an angle. By contrast, the failure mode of the bonded SLJ was shifted to the interfacial failure with 7 degrees of an angle at failure point when they had been exposed to constant temperature profile for three days at 80 °C. Garcia et al. [15] showed diffusion inside adhesive layer causes urethane-urethane H bonds transformation to water-urethane H bonds. This phenomenon is responsible for the plasticization, reduced shear modulus and reduction in joint strength. Similar results observed by da Silva et al. [11].

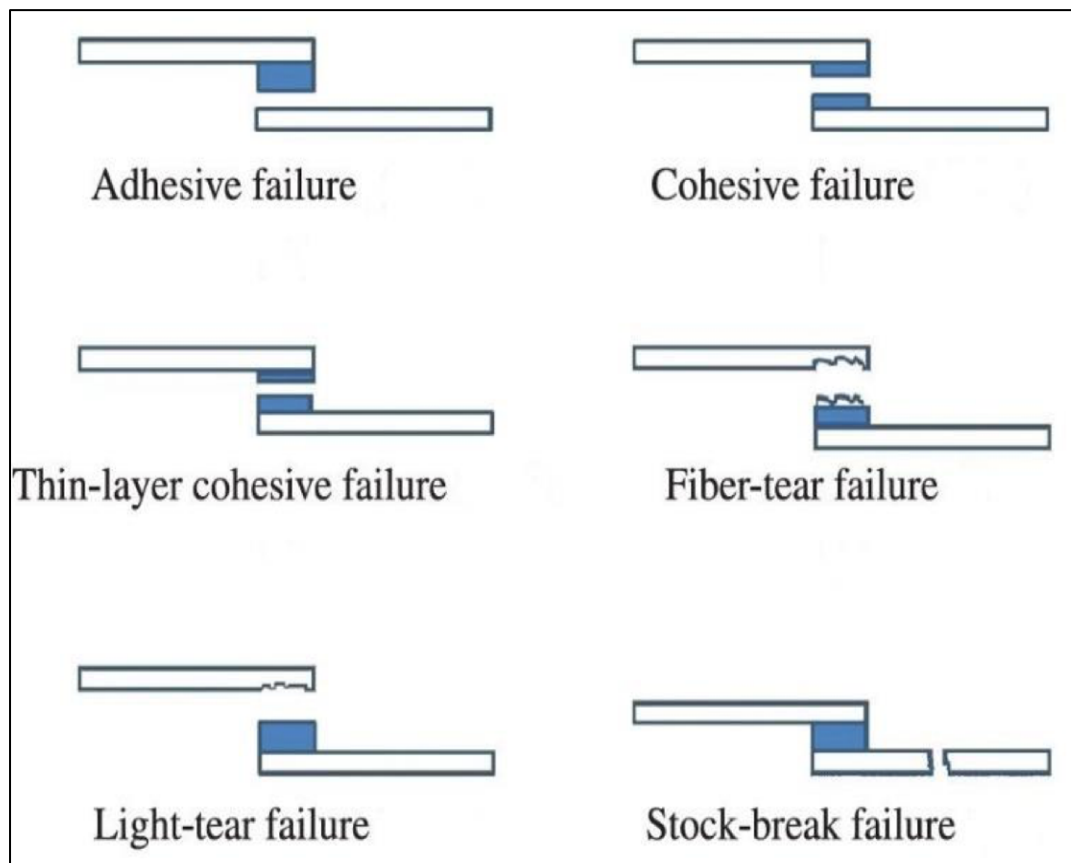


Figure 2.14 Failure Modes in Bonded Joints



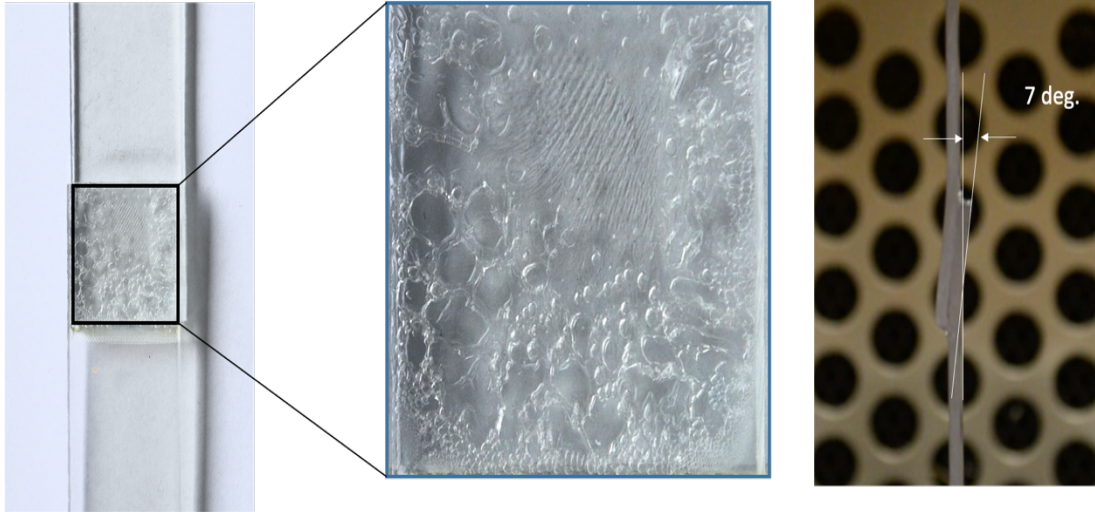


Figure 2.15 Pure Shear Failure Mode in Polycarbonate Joints Bonded at Low Cure Temperature

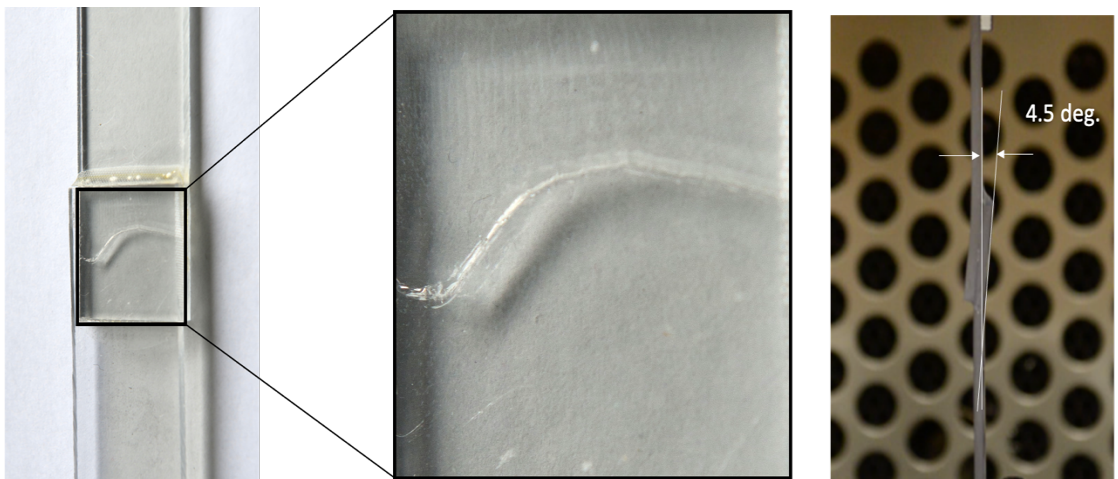


Figure 2.16 Peel Failure Mode in Polycarbonate Joints Bonded at High Cure Temperature



## 2.5 ANOVA

Based on ANOVA data in Table 2.4, the cure temperature (factor A), cure time (factor E), temperature ramp rate (factor D), combinations of temperature ramp rate and cure time (DE), cure temperature and cure time (CE) along with three factor interaction of cure temperature, temperature ramp rate and cure time (CDE) are found to be significant as P-value is less than 0.05 for 95% confidence. Normal plot (Figure 2.16) shows the same significance of same factors and their combinations.

The R-Squared shows how accurate the model is predicting the response values or the measurement of the amount of variation around the mean; R-Squared value that is closer to 1.0 is desirable. In this analysis, the value is equal to 0.9688, which is desirable. Additionally, the difference between Predicted  $R^2$  of 0.9576 and Adjusted  $R^2$  of 0.9412 is less than 0.0164 which is highly favorable.

In addition, Variance Inflation Factor (VIF) with value of 1 indicates an ideal correlation between the regression coefficients or how much the variance around the estimated coefficient is inflated by the lack of orthogonality, in which all the model terms are orthogonal to all other factors in this study. VIFs values more than 10 would raise alarm that present coefficients are poorly estimated because of multi-co-linearity.

An empirical model is presented in coded format to predict joint shear strength based on the statistical analysis of test data. Response equation based on coded factors allows the prediction of response by assigning +1/-1 levels to each independent process variable. In this study, the coded response is given by,

Table 2.6 ANOVA Data for Shear Strength of Baseline Polycarbonate Joints

| Source                   | Sum of Squares | dof | Mean Square | F-value | p-value | VIF |
|--------------------------|----------------|-----|-------------|---------|---------|-----|
| Model                    | 38782731       | 25  | 1551309     | 86.81   | 0       |     |
| Cure Pressure [A]        | 3437           | 1   | 3437        | 0.19    | 0.662   | 1   |
| Press. Ramp Rate [B]     | 10447          | 1   | 10447       | 0.58    | 0.447   | 1   |
| Cure Temperature [C]     | 32712596       | 1   | 32712596    | 1830.61 | 0       | 1   |
| Temp. Ramp Rate [D]      | 863308         | 1   | 863308      | 48.31   | 0       | 1   |
| Cure time [E]            | 3621559        | 1   | 3621559     | 202.66  | 0       | 1   |
| AB                       | 25772          | 1   | 25772       | 1.44    | 0.234   | 1   |
| AC                       | 13965          | 1   | 13965       | 0.78    | 0.38    | 1   |
| AD                       | 4108           | 1   | 4108        | 0.23    | 0.633   | 1   |
| AE                       | 23329          | 1   | 23329       | 1.31    | 0.257   | 1   |
| BC                       | 4411           | 1   | 4411        | 0.25    | 0.621   | 1   |
| BD                       | 17040          | 1   | 17040       | 0.95    | 0.332   | 1   |
| BE                       | 147014         | 1   | 147014      | 8.23    | 0.005   | 1   |
| CD                       | 15113          | 1   | 15113       | 0.85    | 0.361   | 1   |
| CE                       | 472930         | 1   | 472930      | 26.47   | 0       | 1   |
| DE                       | 382825         | 1   | 382825      | 21.42   | 0       | 1   |
| ABC                      | 4897           | 1   | 4897        | 0.27    | 0.602   | 1   |
| ABD                      | 47900          | 1   | 47900       | 2.68    | 0.106   | 1   |
| ABE                      | 178            | 1   | 178         | 0.01    | 0.921   | 1   |
| ACD                      | 222            | 1   | 222         | 0.01    | 0.912   | 1   |
| ACE                      | 82909          | 1   | 82909       | 4.64    | 0.035   | 1   |
| ADE                      | 60878          | 1   | 60878       | 3.41    | 0.069   | 1   |
| BCD                      | 236            | 1   | 236         | 0.01    | 0.909   | 1   |
| BCE                      | 1035           | 1   | 1035        | 0.06    | 0.811   | 1   |
| BDE                      | 4180           | 1   | 4180        | 0.23    | 0.63    | 1   |
| CDE                      | 262442         | 1   | 262442      | 14.69   | 0       | 1   |
| Error                    | 1250881        | 64  |             |         |         |     |
| Total                    | 40033612       | 95  |             |         |         |     |
| R <sup>2</sup>           |                |     | 96.88%      |         |         |     |
| Adjusted R <sup>2</sup>  |                |     | 95.76%      |         |         |     |
| Predicted R <sup>2</sup> |                |     | 94.12%      |         |         |     |

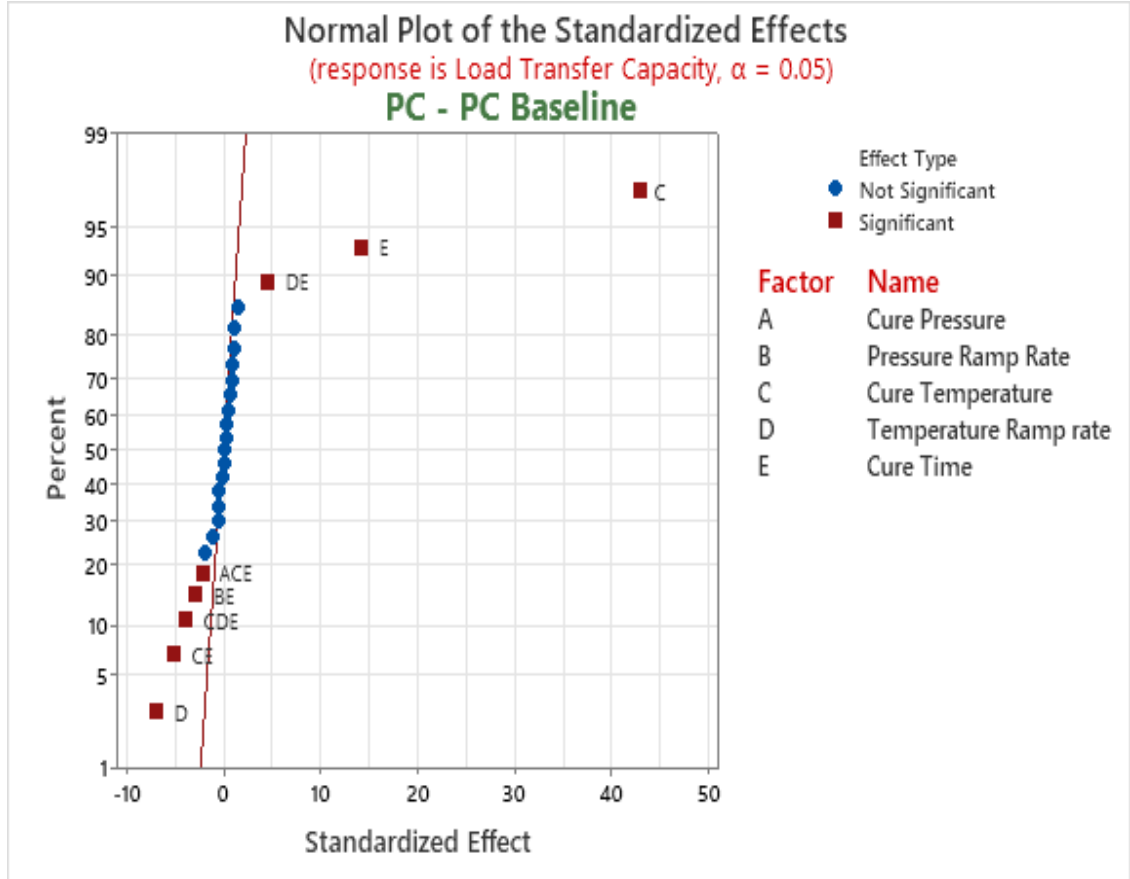


Figure 2.17 Normal Plot for Baseline Shear Strength of Polycarbonate Joints

$$\begin{aligned}
 \text{PC/PC Baseline LTC [N]} = & 3206.5 + 6.0 P + 10.4 R_p + 583.7 T - 94.8 R_t + 194.2 t + \\
 & 16.4 P R_p + 12.1 P T - 6.5 P R_t + 15.6 P t - 6.8 R_p T - 13.3 R_p R_t - 39.1 R_p t + 12.5 T R_t - \\
 & 70.2 T t + 63.1 R_t t + 7.1 P R_p T + 22.3 P R_p R_t + 1.4 P R_p t - 1.5 P T R_t - 29.4 P T t - 25.2 \\
 & P R_t t + 1.6 R_p T R_t + 3.3 R_p T t - 6.6 R_p R_t t - 52.3 T R_t t
 \end{aligned} \quad (1)$$

Equation (1) gives the statistical prediction of the shear strength (N) of Baseline joints that have not been heat cycled. From Figure 2.17 (a) can be observed that residuals follow a normal distribution, as a straight line is fitted through the normal plot of residuals. Figure 2.17 (b) is a plot of the residuals versus the experimental run order,

checks lurking variables that may have influenced the response during the analysis.

Random scatter must be obvious; blocking and randomization of testing would minimize the probability of trends that may invalidate the analysis. Figure 2.18 shows single-variable effect on Baseline shear strength. Lines with positive slopes indicates that increasing that factor would increase joint shear strength; the opposite is true as well. The value of the slope is a measure of how significant the factor is [14].

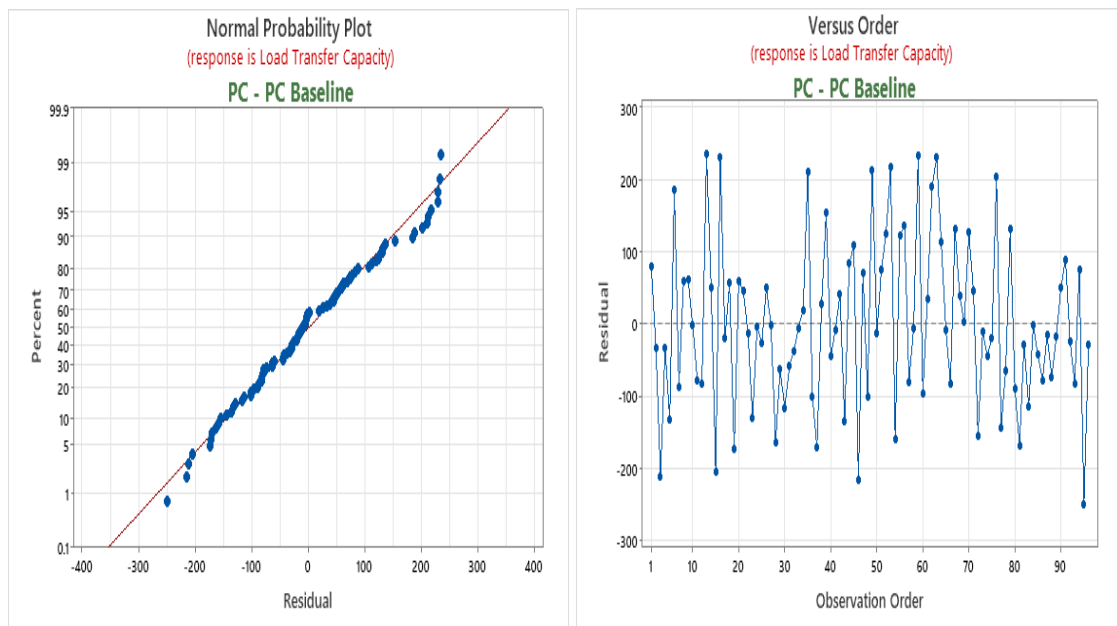


Figure 2.18 Shear Strength of Baseline Polycarbonate Joints  
(a) Normal Plot of residuals (b) Residual vs. Run

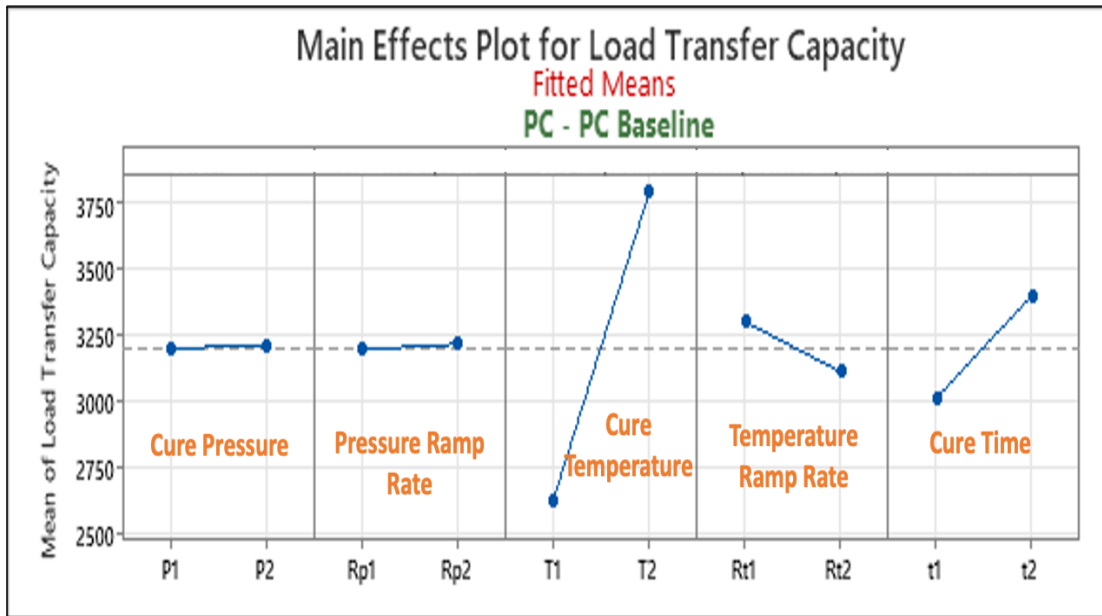


Figure 2.19 Single Variable Effect on Baseline Shear Strength for Polycarbonate Joints

## CHAPTER THREE

### EPOXY ADHESIVE CHARACTERIZATION

#### 3.1 Introduction

Recently, great attention has been focused on using epoxy polymers in different fields such as aerospace, automotive, biotechnology, and electronics, owing to their superior properties. Curing of epoxy polymer materials is nowadays a key technology to achieve low cycle times and subsequently decrease manufacturing costs of both structural and non-structural parts. However, as processes and part geometries get more and more complex, the commonly adopted practice, involving many design iterations until a satisfactory result is obtained, becomes far too expensive. Therefore, it is preferable to experimentally characterize the reaction kinetics to enable performance predictions and eventually optimize the process.

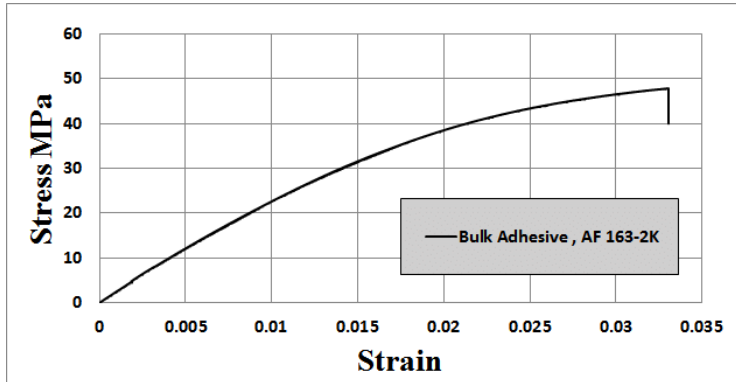
#### 3.2 Epoxy Film Adhesive

The adhesives used in this work are AF 163-2K. This adhesive is produced by 3M Scotch-Weld and is a film adhesive with a knit supporting carrier inside. It presents a film thickness of approximately 0.2 mm in uncured state. It comes with a filler, in the form of reinforcement (fibers), or a thermoplastic knit for bond-line thickness control.

#### 3.3 Curing of Film Adhesive AF163-2K

The formation of a cured epoxy is a two-step process. The first stage in creating a cured epoxy is the preparation of the epoxy resin, or prepolymer, which has not been fully reacted.

Table 3.1 Epoxy Film Adhesive AF163-2K Properties

| Mechanical Properties            | <table><tr><th>Property</th><th>Unit</th><th>Value</th></tr><tr><td>Tensile Strength</td><td>MPa</td><td>45</td></tr><tr><td>Elongation @ break</td><td>%</td><td>500</td></tr><tr><td>100% Modulus</td><td>MPa</td><td>2</td></tr><tr><td>Specific Gravity</td><td></td><td>1.07</td></tr><tr><td>Hardness</td><td>Shore A</td><td>80</td></tr><tr><td>Glass Transition Temperature</td><td>°C</td><td>-36</td></tr></table> | Property                      | Unit  | Value                | Tensile Strength | MPa                     | 45               | Elongation @ break          | % | 500                | 100% Modulus | MPa                              | 2 | Specific Gravity |  | 1.07 | Hardness | Shore A | 80 | Glass Transition Temperature | °C | -36 |
|----------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------|-------|----------------------|------------------|-------------------------|------------------|-----------------------------|---|--------------------|--------------|----------------------------------|---|------------------|--|------|----------|---------|----|------------------------------|----|-----|
|                                  | Property                                                                                                                                                                                                                                                                                                                                                                                                                      | Unit                          | Value |                      |                  |                         |                  |                             |   |                    |              |                                  |   |                  |  |      |          |         |    |                              |    |     |
|                                  | Tensile Strength                                                                                                                                                                                                                                                                                                                                                                                                              | MPa                           | 45    |                      |                  |                         |                  |                             |   |                    |              |                                  |   |                  |  |      |          |         |    |                              |    |     |
|                                  | Elongation @ break                                                                                                                                                                                                                                                                                                                                                                                                            | %                             | 500   |                      |                  |                         |                  |                             |   |                    |              |                                  |   |                  |  |      |          |         |    |                              |    |     |
|                                  | 100% Modulus                                                                                                                                                                                                                                                                                                                                                                                                                  | MPa                           | 2     |                      |                  |                         |                  |                             |   |                    |              |                                  |   |                  |  |      |          |         |    |                              |    |     |
|                                  | Specific Gravity                                                                                                                                                                                                                                                                                                                                                                                                              |                               | 1.07  |                      |                  |                         |                  |                             |   |                    |              |                                  |   |                  |  |      |          |         |    |                              |    |     |
|                                  | Hardness                                                                                                                                                                                                                                                                                                                                                                                                                      | Shore A                       | 80    |                      |                  |                         |                  |                             |   |                    |              |                                  |   |                  |  |      |          |         |    |                              |    |     |
| Glass Transition Temperature     | °C                                                                                                                                                                                                                                                                                                                                                                                                                            | -36                           |       |                      |                  |                         |                  |                             |   |                    |              |                                  |   |                  |  |      |          |         |    |                              |    |     |
| Mechanical Performance           |                                                                                                                                                                                                                                                                                                                                            |                               |       |                      |                  |                         |                  |                             |   |                    |              |                                  |   |                  |  |      |          |         |    |                              |    |     |
| Manufacturer Recommendation      | <table><tr><th>Property</th><th>Range</th></tr><tr><td>Ultimate Temperature</td><td>200 °F – 270 °F</td></tr><tr><td>Ultimate Pressure</td><td>35 psi – 100 psi</td></tr></table>                                                                                                                                                                                                                                             | Property                      | Range | Ultimate Temperature | 200 °F – 270 °F  | Ultimate Pressure       | 35 psi – 100 psi |                             |   |                    |              |                                  |   |                  |  |      |          |         |    |                              |    |     |
| Property                         | Range                                                                                                                                                                                                                                                                                                                                                                                                                         |                               |       |                      |                  |                         |                  |                             |   |                    |              |                                  |   |                  |  |      |          |         |    |                              |    |     |
| Ultimate Temperature             | 200 °F – 270 °F                                                                                                                                                                                                                                                                                                                                                                                                               |                               |       |                      |                  |                         |                  |                             |   |                    |              |                                  |   |                  |  |      |          |         |    |                              |    |     |
| Ultimate Pressure                | 35 psi – 100 psi                                                                                                                                                                                                                                                                                                                                                                                                              |                               |       |                      |                  |                         |                  |                             |   |                    |              |                                  |   |                  |  |      |          |         |    |                              |    |     |
| Chemical Composition             | <table><tr><th colspan="2">AF163-2K Chemical Composition</th></tr><tr><td colspan="2">Resin: Epoxy</td></tr><tr><td colspan="2">Hardener: Dicyandiamide</td></tr><tr><td colspan="2">1,1'-(4-Methyl-M-Phenylene)</td></tr><tr><td colspan="2">Adipic Dihydrazide</td></tr><tr><td colspan="2">Polymeric Epoxy Reaction Product</td></tr></table>                                                                              | AF163-2K Chemical Composition |       | Resin: Epoxy         |                  | Hardener: Dicyandiamide |                  | 1,1'-(4-Methyl-M-Phenylene) |   | Adipic Dihydrazide |              | Polymeric Epoxy Reaction Product |   |                  |  |      |          |         |    |                              |    |     |
| AF163-2K Chemical Composition    |                                                                                                                                                                                                                                                                                                                                                                                                                               |                               |       |                      |                  |                         |                  |                             |   |                    |              |                                  |   |                  |  |      |          |         |    |                              |    |     |
| Resin: Epoxy                     |                                                                                                                                                                                                                                                                                                                                                                                                                               |                               |       |                      |                  |                         |                  |                             |   |                    |              |                                  |   |                  |  |      |          |         |    |                              |    |     |
| Hardener: Dicyandiamide          |                                                                                                                                                                                                                                                                                                                                                                                                                               |                               |       |                      |                  |                         |                  |                             |   |                    |              |                                  |   |                  |  |      |          |         |    |                              |    |     |
| 1,1'-(4-Methyl-M-Phenylene)      |                                                                                                                                                                                                                                                                                                                                                                                                                               |                               |       |                      |                  |                         |                  |                             |   |                    |              |                                  |   |                  |  |      |          |         |    |                              |    |     |
| Adipic Dihydrazide               |                                                                                                                                                                                                                                                                                                                                                                                                                               |                               |       |                      |                  |                         |                  |                             |   |                    |              |                                  |   |                  |  |      |          |         |    |                              |    |     |
| Polymeric Epoxy Reaction Product |                                                                                                                                                                                                                                                                                                                                                                                                                               |                               |       |                      |                  |                         |                  |                             |   |                    |              |                                  |   |                  |  |      |          |         |    |                              |    |     |
|                                  |                                                                                                                                                                                                                                                                                                                                                                                                                               |                               |       |                      |                  |                         |                  |                             |   |                    |              |                                  |   |                  |  |      |          |         |    |                              |    |     |
|                                  |                                                                                                                                                                                                                                                                                                                                                                                                                               |                               |       |                      |                  |                         |                  |                             |   |                    |              |                                  |   |                  |  |      |          |         |    |                              |    |     |

The most common epoxy resin prepolymer used in industry today is formed from the reaction of bisphenol-A and epichlorohydrin, shown in Figure 3.1, in which the product contains the oxirane group.

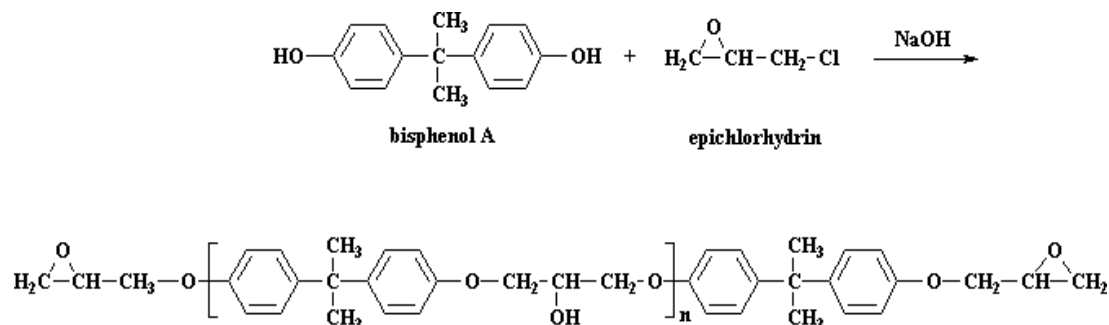


Figure 3.1 Reaction between bisphenol A and epichlorohydrin to form epoxy resin (prepolymer)

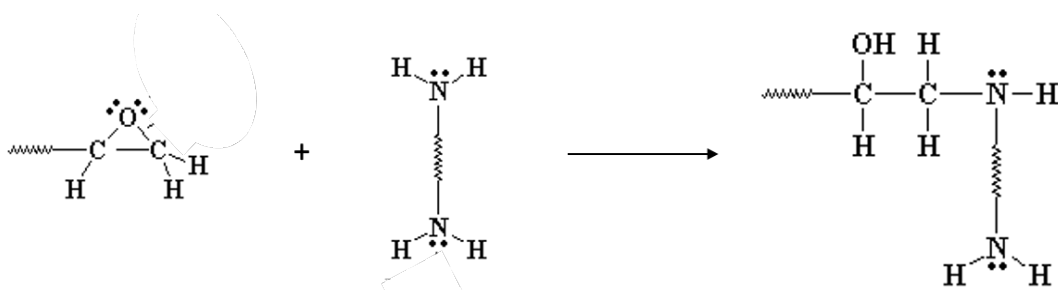


Figure 3.2 Cure reaction of epoxy resin with amine hardener

These epoxy resins are cross-linked either in a catalytic homo polymerization reaction or using co-reactants. During the curing reaction, the liquid resin reacts at the oxirane site to form the solid thermoset. Several cross-linking (curing) agents are available for use with epoxy resins, with the most popular being polyamines, anhydrides,



polyamides, and catalytic curing agents (which do not act directly as cross-linking agents). In the epoxy cure reaction, the speed of cure is controlled by the type of reactant used as well as cure temperature. In the most common cure reaction, addition reaction using an amine as a hardener, two epoxy groups bond to one amine group, shown in Figure 3.2. This is the basis for the formation of the final 3D network in Figure 3.3. As the curing process uses a co- reactant, the appropriate amount of hardener must be used to ensure full reaction. One of the associated complications during manufacturing of epoxy resins is the difficulty resulting from the need for precise measurement of the ratio between resin and hardener to achieve full cure and fully realized material properties.

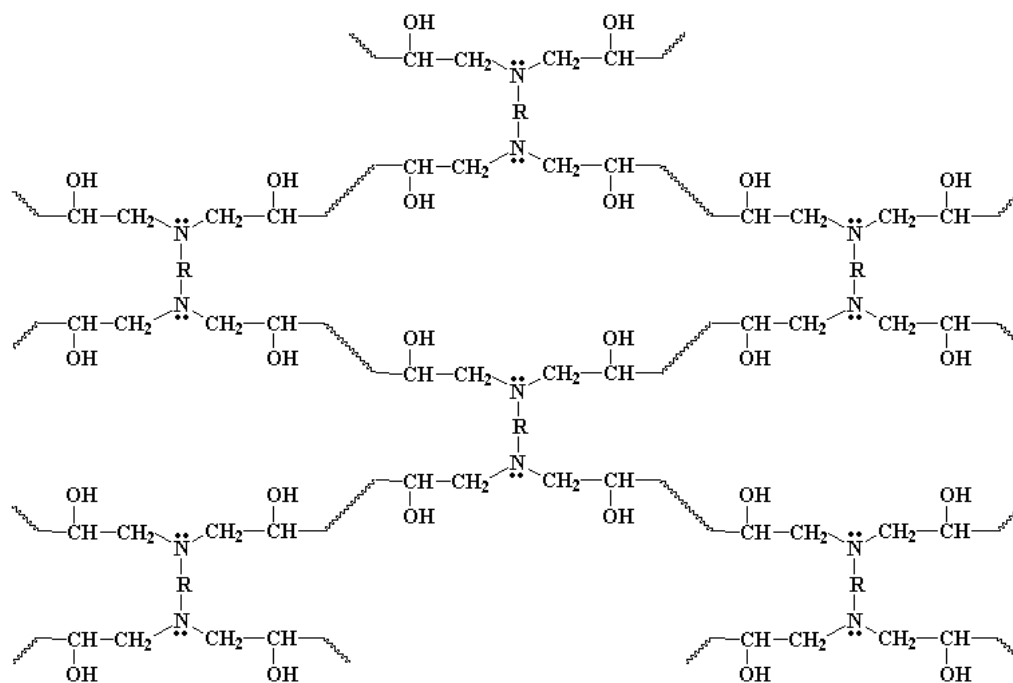


Figure 3.3 Cross-Linked Epoxy

### 3.4 Defining the Stages of Cure

The cure of thermosets refers to the chemical process that is the cross-linking of polymer chains to form a rigid and infinite 3D network of increased molecular weight as the liquid resin is transformed into the solid thermoset, as described for epoxy and polyester in the previous section. During cure there is a change in chemical structure and properties that results in a secondary change in physical properties, which is irreversible in thermosetting polymers.

The stages of cure are shown in the flow chart in Figure 3.4. From the liquid resin stage, the start of the cure process is initiated either by heat, irradiation, or a chemical reaction. As the exothermic reaction proceeds, polymer cross-links form continuously and eventually create an infinite network. This is described as the gelation point. At this point, the material changes from the viscous liquid to the elastic gel or rubber state and the polymer will cease to flow. As cure proceeds, the number of 3D crosslinks and the molecular weight of the polymer will continue to increase until the thermoset reaches the solid state, which is described as vitrification. Vitrification has been defined as the point at which the glass transition temperature and cure temperature are equal. The polymer then proceeds to the end of cure, at which point no new crosslinks can be formed at that temperature. Further heating can either result in further cure of the material or degradation, in which the polymer chains become damaged by scission. In general, a higher cure temperature will result in an increase in rate of reaction for cure.

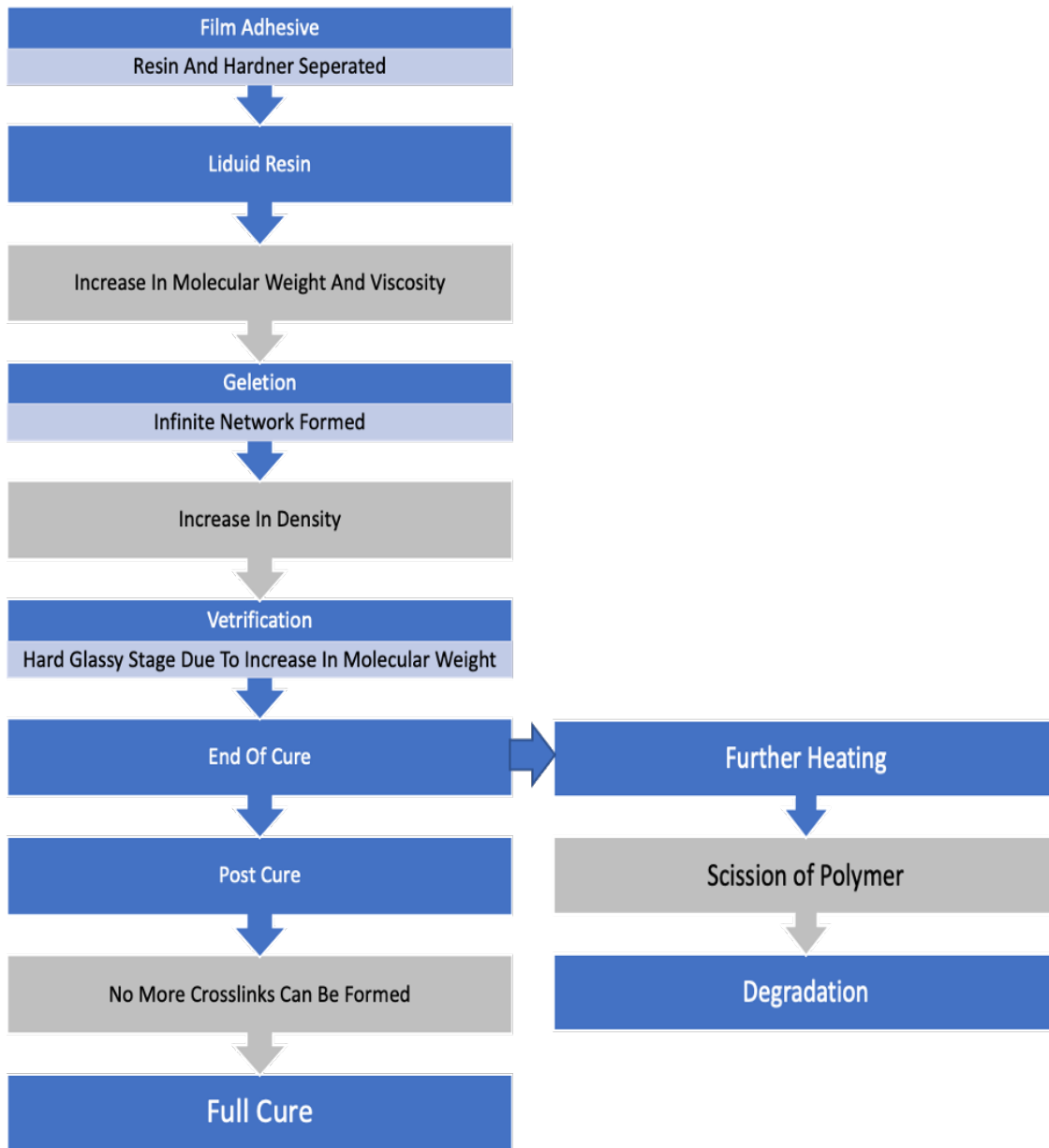


Figure 3.4 Flow Diagram of The Stages of Thermoset Cure

### 3.5 The Glass Transition Temperature ( $T_g$ ) indicator of cure

One of the material properties most regularly measured by thermal analysis is the glass transition temperature, or  $T_g$ , the glass transition region occurs over a temperature range and marks the region in which the behavior of a material changes from glassy to rubbery with increasing temperature. In the glassy state, local molecular mobility is restricted, where chain rotation cannot occur due to insufficient thermal energy and as a result its structure is frozen into position. As a material is heated, translational and rotational motion become possible. The  $T_g$  is a point within this transition region, frequently referred to in the literature as the alpha transition, that is used as a means of usefully representing this change with temperature. The  $T_g$  is often defined as the onset of long-range segmental motion.

As the temperature is increased through the  $T_g$ , chemically crosslinked, thermosetting polymers will reach a rubbery plateau whilst thermoplastics will begin to flow. Further heating past the  $T_g$  of a thermoset polymer result in irreversible damage to the chemical crosslinks and therefore degradation, unlike thermoplastics which eventually achieve melt when heated above the  $T_g$ . The  $T_g$  is therefore an important thermal property of composite materials which is frequently used to help define a suitable service temperature, given by an offset from the measured  $T_g$ , (in addition to considerations for the environmental performance of the material).

During cure, thermosetting polymers undergo many physical property changes associated with the chemical changes (i.e., increased crosslinking) that result from the cure process, including an increase in  $T_g$ . Consequently, the  $T_g$  can be used as a convenient indicator of the cure state of a composite material.

In the initial liquid resin stage of the cure process, the  $T_g$  is lower than the cure temperature,  $T_{cure}$ . As cure proceeds up to the gelation point, the elastic modulus remains low, while the viscosity of the resin undergoes a drastic increase. Once the resin reaches the gel point, the glass transition temperature rises sharply. With increasing degree of cure, also known as conversion, the glass transition temperature continues to rise until the vitrification point, when  $T_g = T_{cure}$  and the material moves from the rubbery to the glassy state. Full cure is defined as the stage at which the  $T_g$  has reached a constant value. As the glass transition temperature continues to increase throughout the cure process, it can be used as a reliable indicator of the degree of cure of a polymer.

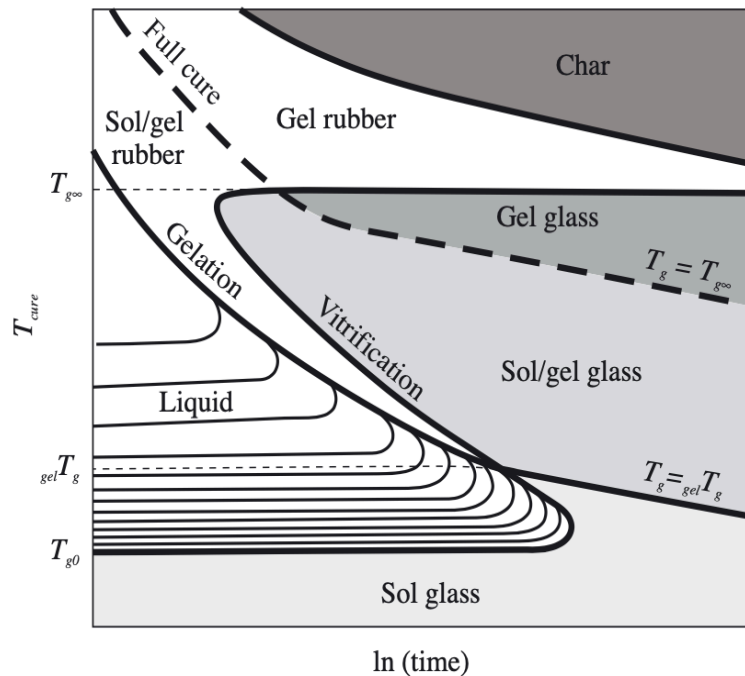


Figure 3.5 Time-Temperature-Transformation (TTT) Cure Diagram for An Epoxy System

### 3.5.1 Relationship Between $T_g$ and Degree of Cure ( $\alpha$ )

The glass transition temperature ( $T_g$ ) is one of the most important parameters of an epoxy system.  $T_g$  determines the temperature boundary of significant changes in the enthalpic, viscoelastic, dilatometric etc. The relationship between  $T_g$  and conversion degree in the curing reaction ( $\alpha$ ) of thermosetting materials is a central concept in analysing cure phenomena. The relevance of  $T_g$  to properties of material is based on the following: [a] processing of a reactive material must be performed at temperatures above the value of  $T_g$  of uncured material ( $T_{g0}$ ). [b] the value of  $T_g$  at full conversion of a thermoset ( $T_{g\infty}$ ) is related to the upper temperature limit of the glass-converted material as shown in Figure 8. The relationship between  $T_g$  and  $\alpha$  determines when vitrification occurs during cure, for which  $T_g$  equals the cure temperature ( $T_{cure}$ ). At a given  $T_{cure}$ , the reaction of a thermosetting material proceeds generally at a rate dictated by chemical kinetics if  $T_g$  is less than  $T_{cure}$ . However, if  $T_g$  is higher than  $T_{cure}$ , the reaction rate is controlled by diffusion. The empirical DiBenedetto equation [14] gives relationship between  $T_g$  and  $\alpha$  for a wide variety of thermosets,

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda \alpha}{1 - (1 - \lambda) \alpha} \quad (2)$$

$\lambda = \Delta C_{p\infty} / \Delta C_{p0}$  (Structure-dependent parameter with value between 0-1.  $\lambda$  value for AF163-2K is 0.422 (from manufacture's specification).

### 3.6 Experimental Procedure and Test Setup

#### 3.6.1 DMA Sample Preparation

Adhesive film AF163-2K was cured for 32-different combinations of autoclave processes. Film 5" X 5" was placed inside parchment paper in vacuum bag. DMA sample specimen of 20 mm in length and 10 mm width were cut from the big cured adhesive film as shown in Figure 3.6. Illustration of cure cycle (Autoclave process ID 1:  $T_1$ ,  $R_{t1}$ ,  $P_1$ ,  $R_{p1}$ ,  $t_1$ ) along with behavior of degree of cure and crosslinking in the epoxy system is shown in Figure 3.7.

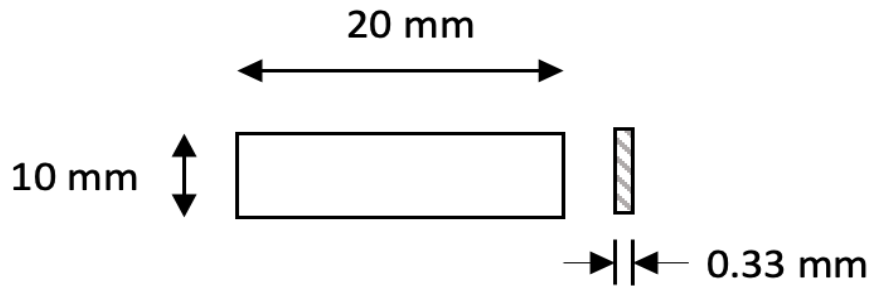


Figure 3.6 DMA Sample Illustration

#### 3.6.2 Measurement of the $T_g$ using DMA

DMA is a popular technique due to its relative speed and high sensitivity to the glass transition. This technique takes advantage of the change in modulus and damping properties of a material at the glass transition temperature, where the onset of chain

movement results in an increase in free volume, allowing molecular motion to occur more freely (Figure 3.7). In this test method, the specimen is placed inside the DMA furnace and subjected to a controlled heating profile as shown in Figure 3.9. The sample can be clamped inside the furnace in several deformation modes, including single-cantilever, dual-cantilever, tension and three-point bend. Throughout the test, the specimen is subjected to sinusoidal mechanical deformation that induces a stress,  $\sigma$ , which results in a corresponding strain,  $\epsilon$ , which is out of phase with the sinusoidal stress by angle,  $\delta$ . The phase lag between stress and strain occurs because of the viscoelastic response of the material.

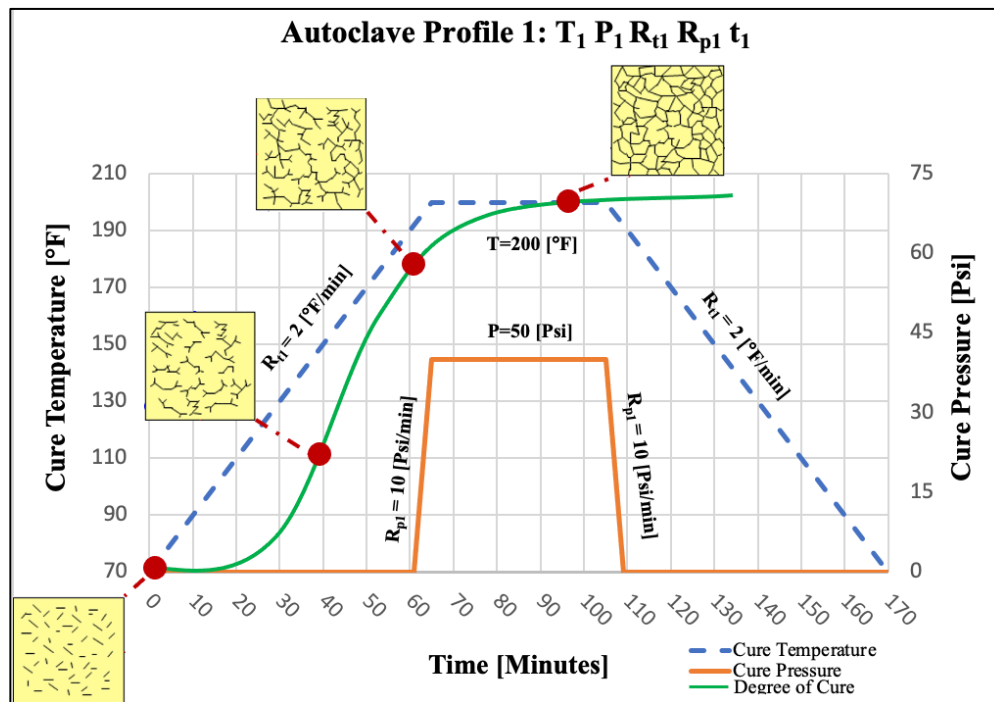


Figure 3.7 Autoclave Profile with Progress in Cure Illustration



During analysis, the storage modulus, loss modulus and tan delta are presented on separate axes as a function of temperature. The glass transition is directly related to the crosslink density and storage modulus and can be seen as a step change in the storage modulus of the material on this graph. This is shown in Figure 3.10, where the  $T_g$  is taken as the inflection point of this curve. The values of loss modulus, which represents the energy dissipated as heat, and tan delta, which represents damping, are also presented against temperature on the graph in Figure 3.11, where the glass transition temperature may also be interpreted as either the peak of the loss modulus curve or the peak of the tan delta curve. In addition to these three analysis points, the onset point of the storage modulus curve is occasionally used as a value for  $T_g$ .



Figure 3.8 Dynamic Mechanical Analyzer

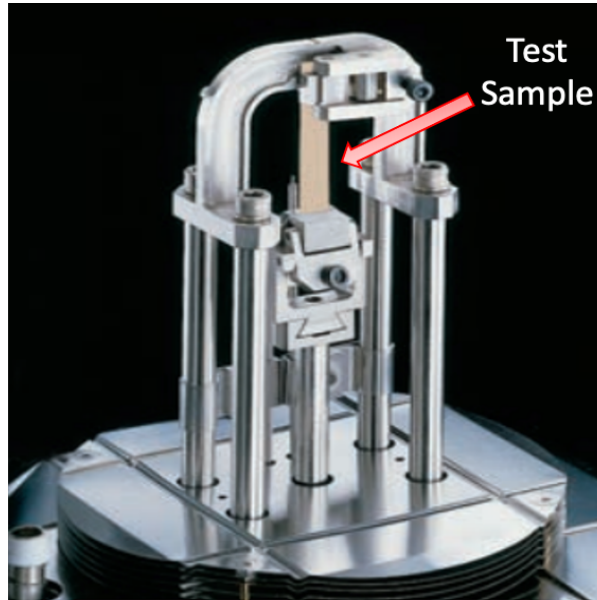


Figure 3.9 DMA test setup

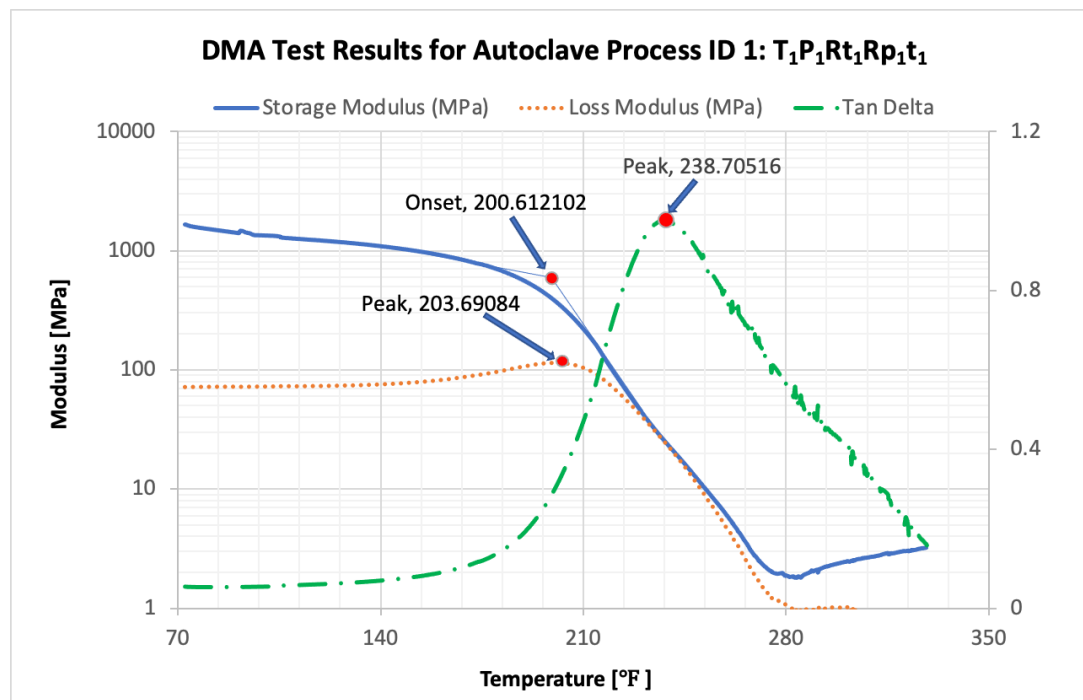


Figure 3.10 DMA Result Illustration

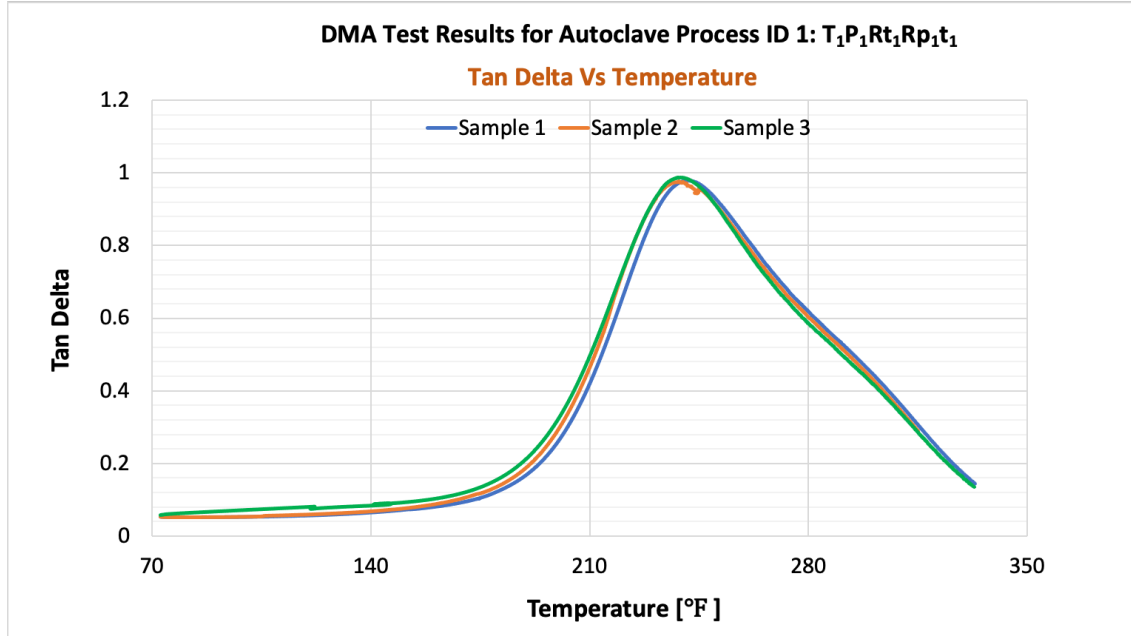


Figure 3.11 DMA Results for Autoclave ID 1 for Three Samples

### 3.6.3 Glass Transition Temperature at Full Conversion

Dynamic mechanical analysis (DMA) experiments were carried out in a TA Instruments Q800. Force and displacement calibration were done according to manufacturer recommendations. The complex Young's modulus ( $E^*$ ) of the cured AF163-2K epoxy film was measured using a DMA over the temperature range 20 to 170°C in an air environment with sinusoidal displacement. Measurements were at a fixed frequency of 1 Hz with a temperature ramp rate of 1°C/min. Three samples for each of 32 different autoclave cure conditions were tested. The glass transition temperature was calculated as the peak of the tangent delta signal. Sample size was 10mm in width and 20 mm in length. The fixture directly gripped the specimen approximately 5 mm from the end of the specimen length.

The  $T_g$  value of uncured epoxy film  $T_{g0} = 28$  [°F] is obtained from tan delta curve of DMA test results. For  $T_g$  value at full conversion of an epoxy film ( $T_{g\infty}$ ) series of DMA tests are carried out over cure temperature ( $T_{\text{cure}}$ ) range from 180 to 300 [°F] holding all other cure parameters constant. Highest value of  $T_g$  on the  $T_{\text{cure}}$  Vs  $T_g$  graph is considered as  $T_{g\infty} = 310$  [°F] as shown in Figure 3.12.

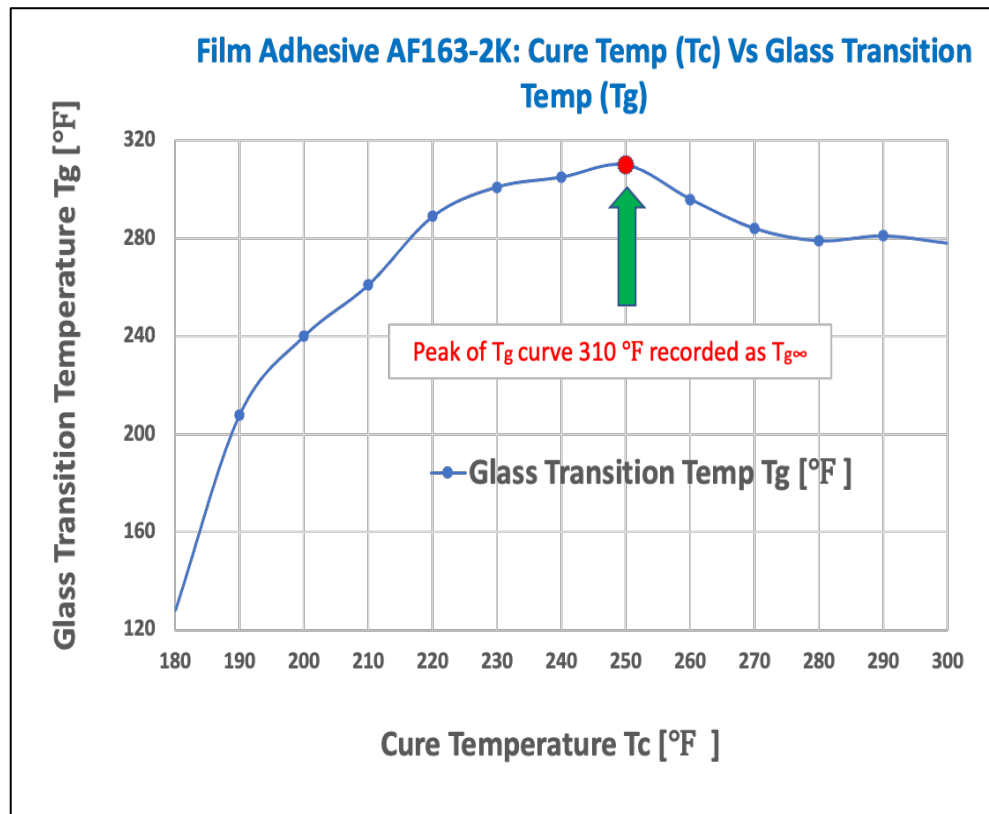


Figure 3.12 Cure Temp. ( $T_{\text{cure}}$ ) Vs Glass Transition Temperature ( $T_g$ ) Graph for AF163-2K Epoxy Film Adhesive

### 3.7 Results and Discussion

In this section experimental results for DMA testing are presented and discussed. Figure 3.13 shows glass transition temperature ( $T_g$ ) for all autoclave bonding process for ambient and after environmental loading. Figure 3.14-3.17 shows effect of one autoclave process variable on glass transition temperature ( $T_g$ ) when other four autoclave process variables remained same.

Figure 3.13 gives comparative overview of glass transition temperature ( $T_g$ ) of 32 autoclave processes designed with all possible combination of five process variables. Baseline static LTC is higher for all autoclave process when compared to static LTC after cyclic heat at high relative humidity. High glass transition temperature ( $T_g$ ) of 291.7 °F was observed autoclave process variables of cure temperature  $T_2 = 260$  °F, cure pressure  $P_2 = 100$  Psi, temperature ramp rate  $R_{t1} = 2$  °F/min, pressure ramp rate  $R_{p1} = 10$  Psi/min, cure time  $t_1 = 40$  min. Lower glass transition temperature ( $T_g$ ) of 187.8 °F was observed autoclave process variables of cure temperature  $T_1 = 200$  °F, cure pressure  $P_1 = 50$  Psi, temperature ramp rate  $R_{t2} = 7$  °F/min, pressure ramp rate  $R_{p2} = 15$  Psi/min, cure time  $t_1 = 40$  min.

Figure 3.14 shows Glass Transition Temperature ( $T_g$ ) of AF163-2K epoxy adhesive is higher for combination of low cure temperature ( $T_1 = 200$  °F) and high cure time ( $t_2 = 100$  min) when compared to combination of low cure temperature ( $T_1 = 200$  °F) with low cure time ( $t_1 = 40$  min), for all autoclave processes when other variables ( $P$ ,  $R_t$ ,  $R_p$ ) remained same.

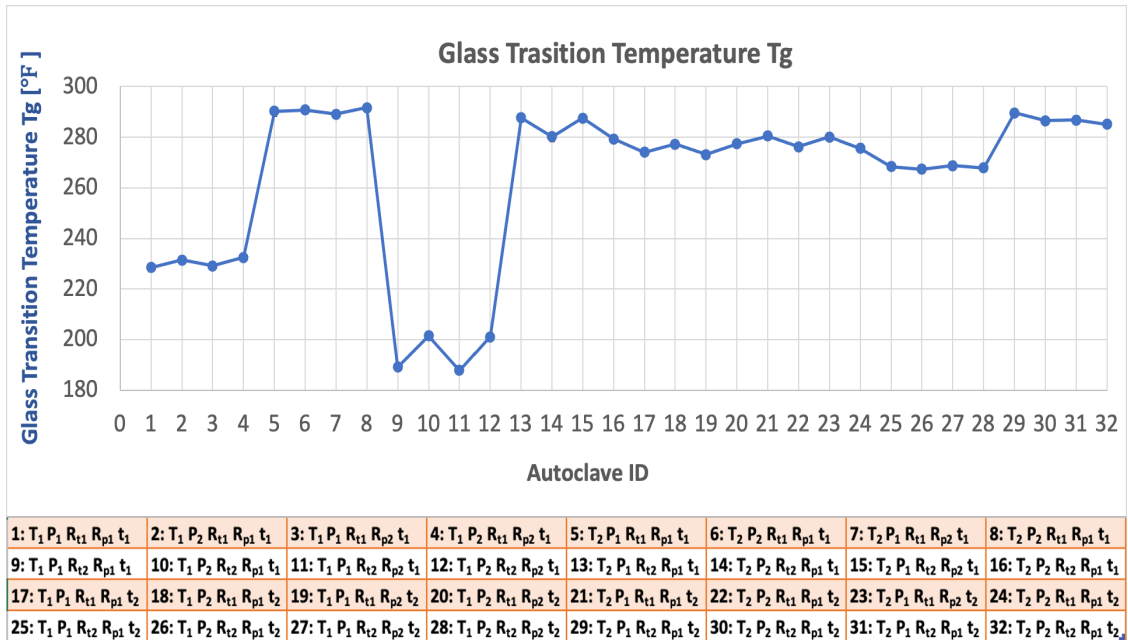


Figure 3.13 Glass Transition Temperature (T<sub>g</sub>) for All Autoclave Process Combinations

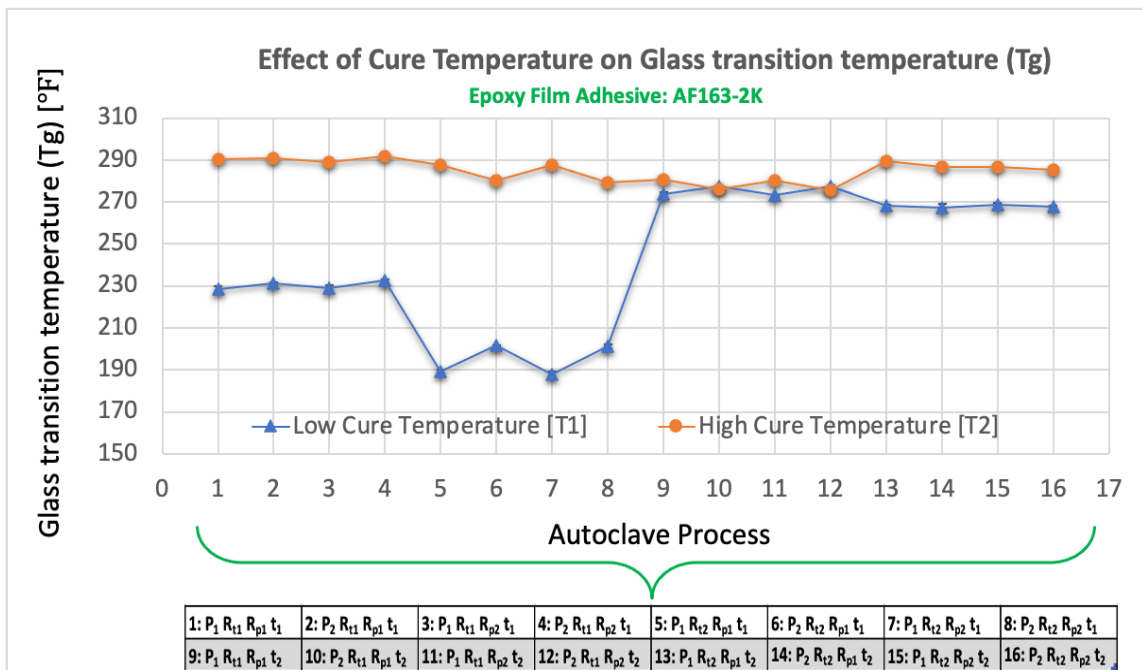


Figure 3.14 Effect of Cure Temperature on Glass Transition Temperature (T<sub>g</sub>) of Epoxy Adhesive AF163-2K

Figure 3.15 shows effect of cure pressure on Glass Transition Temperature ( $T_g$ ) when other process variables remained same ( $T$ ,  $R_t$ ,  $R_p$ ,  $t$ ). Higher cure pressure has positive effect on the Glass Transition Temperature ( $T_g$ ) of epoxy adhesive.

Figure 3.16 shows effect of temperature ramp rate on Glass Transition Temperature ( $T_g$ ) when other process variables remained same ( $T$ ,  $P$ ,  $R_p$ ,  $t$ ). It is observed that temperature ramp rate interacts with cure temperature. Its combination with high cure temperature and high cure time has detrimental effect on the cross-linking formation in the adhesive.

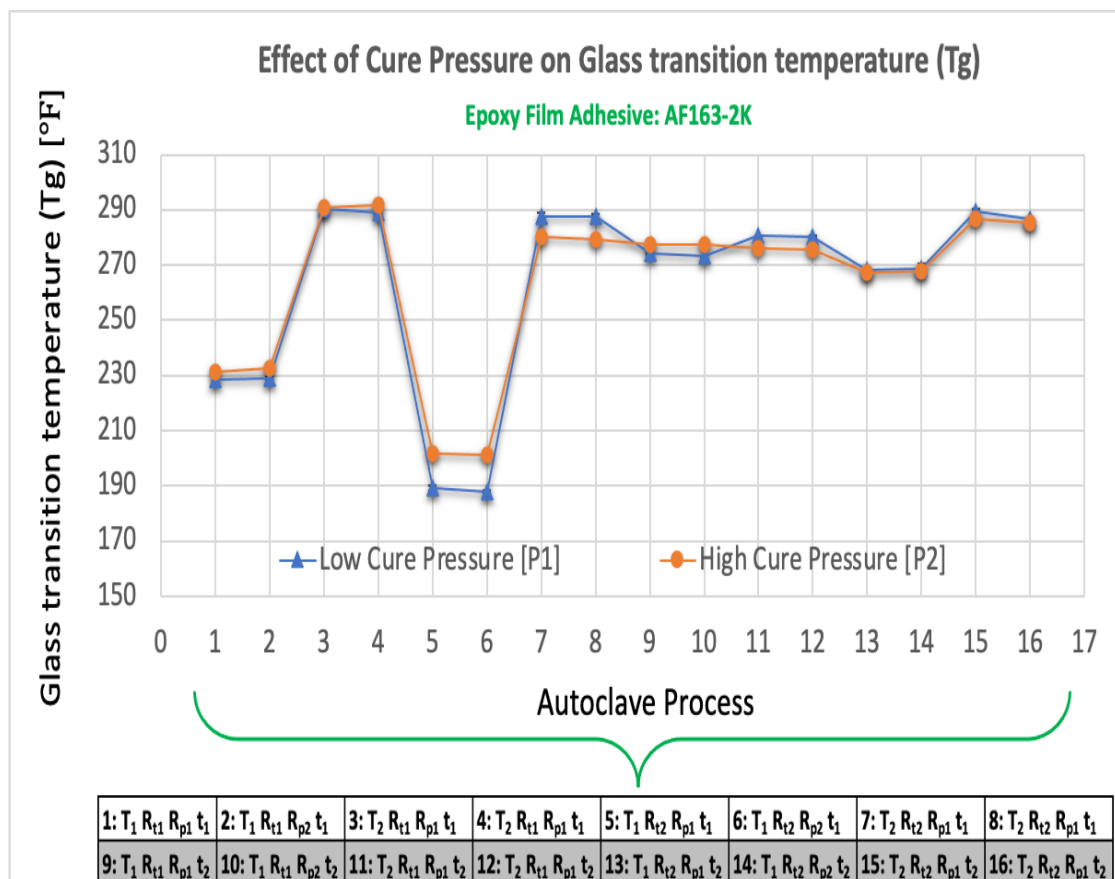


Figure 3.15 Effect of Cure Pressure on Glass Transition Temperature ( $T_g$ ) of Epoxy Adhesive AF163-2K

Figure 3.17 shows effect of cure time on Glass Transition Temperature ( $T_g$ ), when other process variables remained same ( $P$ ,  $T$ ,  $R_t$ ,  $R_p$ ). It is observed that for most of autoclave processes, high soak time ( $t_2 = 100$  min) have higher Glass Transition Temperature ( $T_g$ )

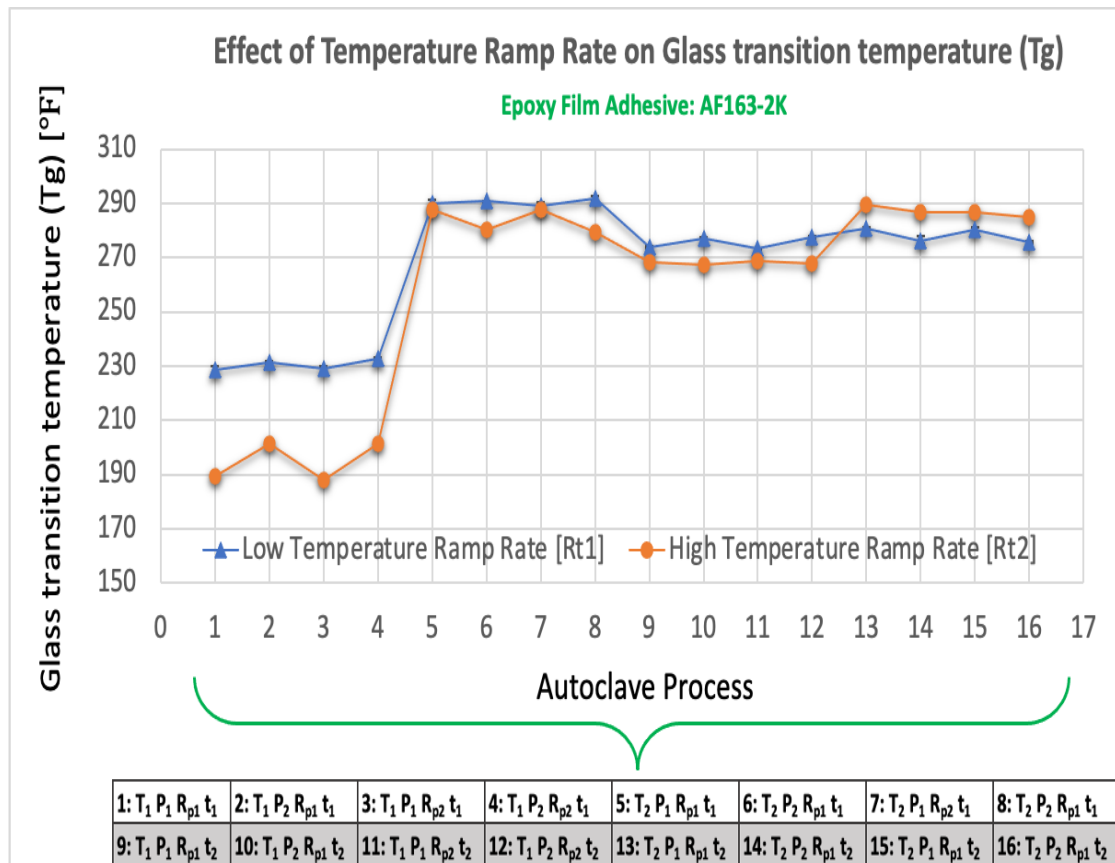


Figure 3.16 Effect of Temperature Ramp Rate on Glass Transition Temperature ( $T_g$ ) of Epoxy Adhesive AF163-2K



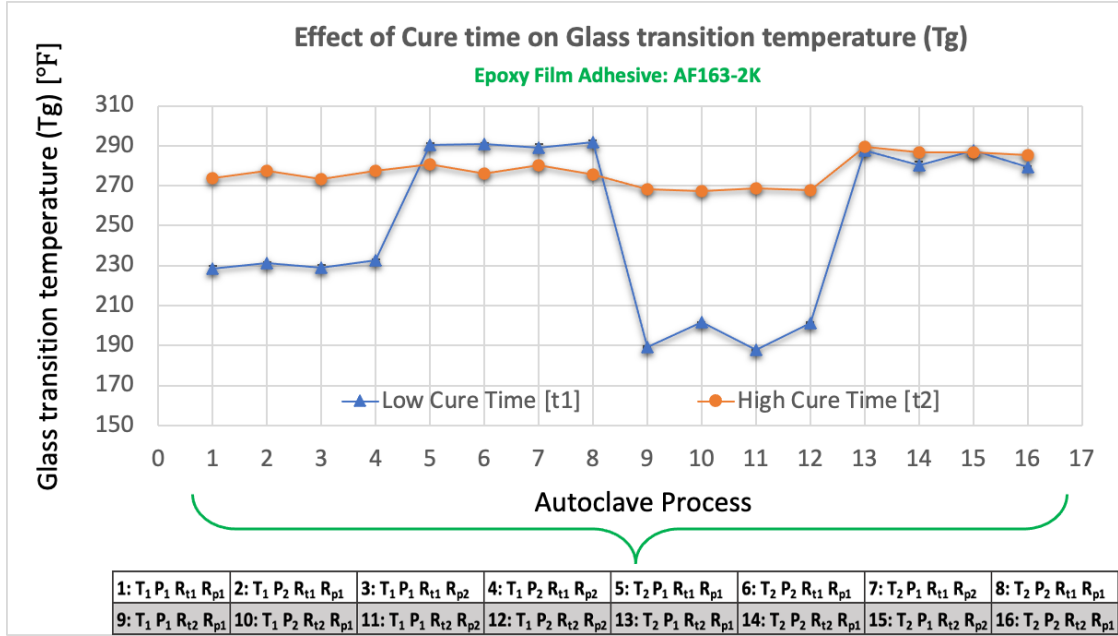


Figure 3.17 Effect of Cure Time on Glass Transition Temperature ( $T_g$ ) of Epoxy Adhesive AF163-2K

### 3.8 Effect of Cure Pressure

The results in previous section showed that, to some extent, the increased curing pressure could improve the cross-linking densities of the cured products. Yi Xu et al. [63] explained effect of cure pressure on epoxy adhesive proposed curing process is shown in Figure 3.18. The epoxies rings opened to form carbonyl groups and hydroxyl groups during the curing process. The increased curing pressure caused more hydroxyl groups to dehydrate to form carbonyl structures. The existence of the intermolecular hydrogen bonding formed by the hydroxyl groups and carbonyl groups increased the interaction of the polymer chains, thus the polymer chains were packed more closely, and the degree of the cross-linking was the highest for epoxy film adhesive cured at high cure pressure.

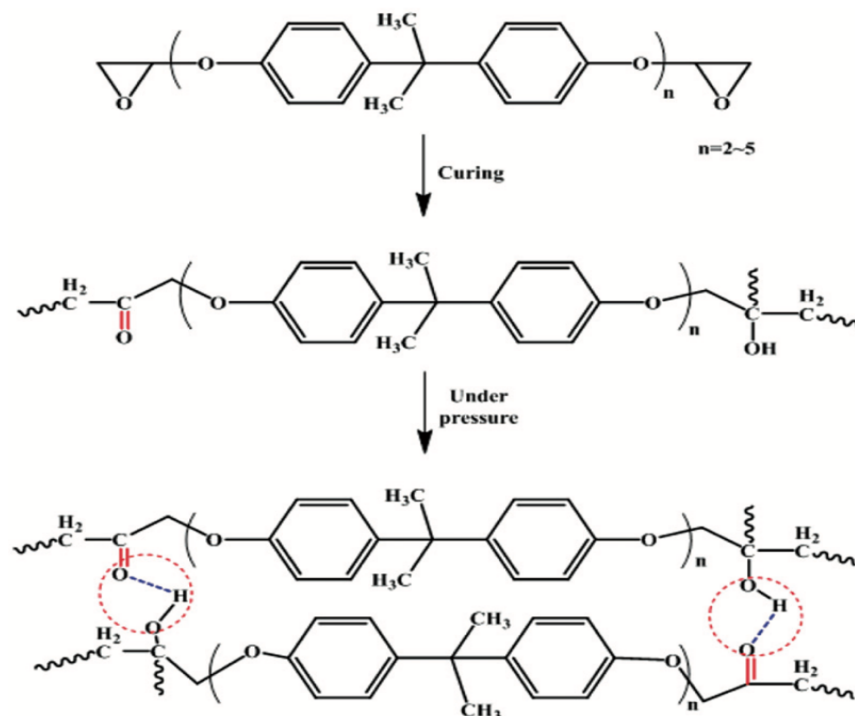


Figure 3.18 Cross-linking and Hydrogen Bonding in the Cured Epoxy

Fourier transform infrared (FTIR) spectra are shown in the figure 3.19 for film epoxy adhesive cured at different pressure. The characteristic peaks for the end group epoxy rings at  $914\text{ cm}^{-1}$  disappeared and the characteristic peak for hydroxyl groups at  $1409\text{ cm}^{-1}$  appeared for cured polymers which indicates that the film adhesive is cured. In addition, there was characteristic peak at  $1718\text{ cm}^{-1}$  for carbonyl groups appeared for these cured polymers. The reason was explained by Yi Xu et al. [63] is hydroxyl dehydration reaction. Also, variation in the peak size, suggested that the curing pressure have relationships with the formation of the carbonyl groups.

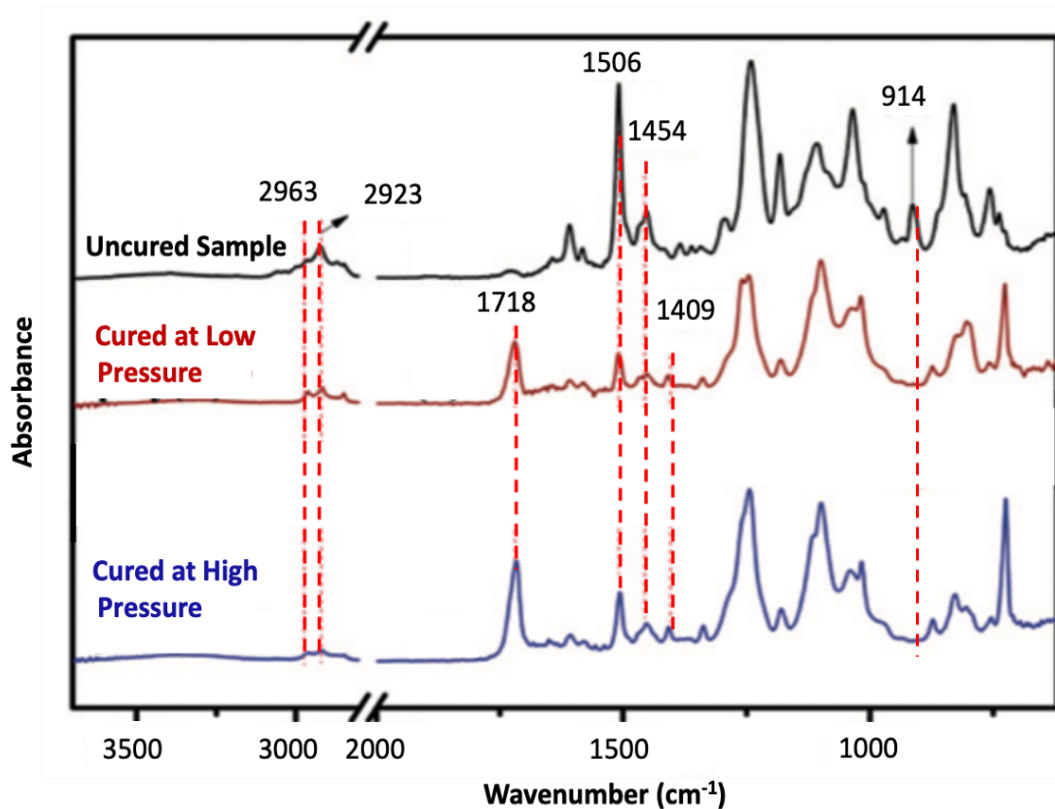


Figure 3.19 FTIR Spectra for Epoxy Adhesive Cured at Different Curing Pressure

### 3.9 ANOVA

Based on ANOVA data in Table 3.2, the cure temperature (factor C), Cure time (factor E), interaction CE along with other factors and interactions found to be significant as P-value is less than 0.05 for 95% confidence. Normal plot (Figure 3.20) shows the significance of factors and interactions.

The R-Squared shows how accurate the model is predicting the response values or the measurement of the amount of variation around the mean; R-Squared value that is closer to 1.0 is desirable. In this analysis, the value is equal to 0.9995, which is good.

Additionally, the difference between Predicted  $R^2$  of 0.9988 and Adjusted  $R^2$  of 0.9992 is less than 0.0004 which is favourable.

In addition, Variance Inflation Factor (VIF) with value of 1 indicates an ideal correlation between the regression coefficients or how much the variance around the estimated coefficient is inflated by the lack of orthogonality, in which all the model terms are orthogonal to all other factors in this study. VIFs values more than 10 would raise alarm that present coefficients are poorly estimated because of multi-co-linearity.

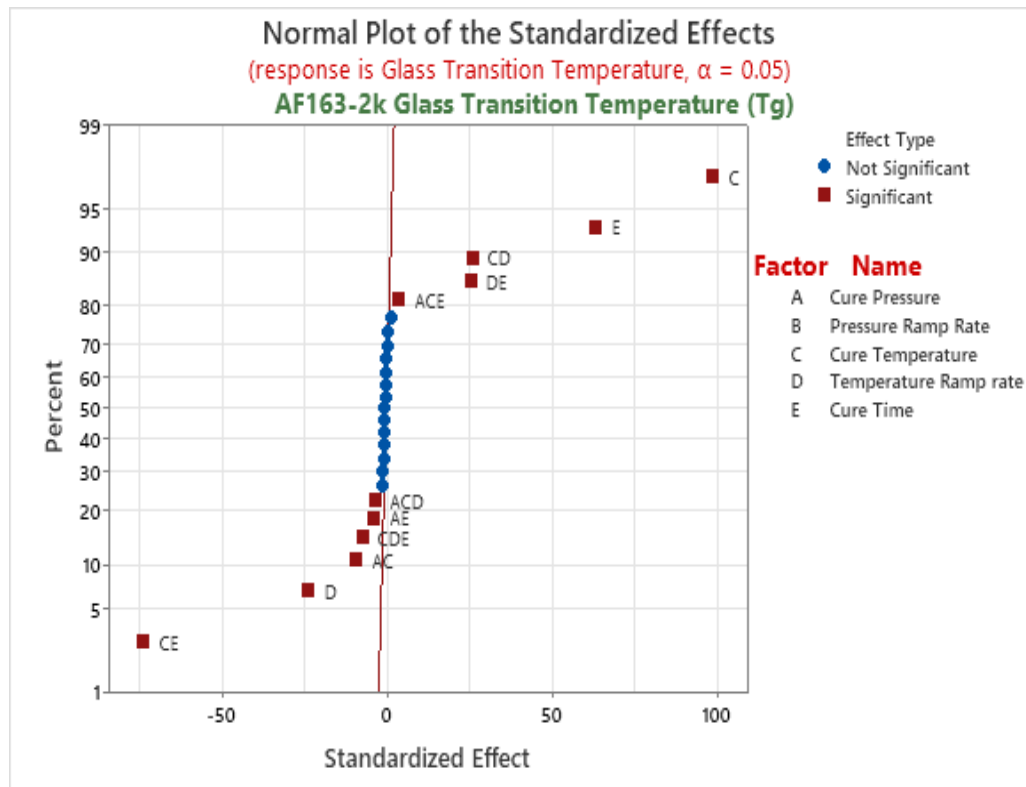


Figure 3.20 Normal Plot for Glass Transition Temperature (Tg)

Table 3.2 ANOVA Data for Glass Transition Temperature ( $T_g$ )

| Source               | Sum of Squares | dof | Mean Square | F-value | p-value | VIF |
|----------------------|----------------|-----|-------------|---------|---------|-----|
| Model                | 94938.1        | 25  | 3797.5      | 854.09  | 0       |     |
| Cure Pressure [A]    | 11.7           | 1   | 11.7        | 2.64    | 0.109   | 1   |
| Press. Ramp Rate [B] | 3.9            | 1   | 3.9         | 0.88    | 0.35    | 1   |
| Cure Temperature [C] | 43514.1        | 1   | 43514.1     | 9786.65 | 0       | 1   |
| Temp. Ramp Rate [D]  | 2486.2         | 1   | 2486.2      | 559.17  | 0       | 1   |
| Cure time [E]        | 17923.5        | 1   | 17923.5     | 4031.14 | 0       | 1   |
| AB                   | 2.2            | 1   | 2.2         | 0.49    | 0.488   | 1   |
| AC                   | 378.5          | 1   | 378.5       | 85.14   | 0       | 1   |
| AD                   | 2.3            | 1   | 2.3         | 0.52    | 0.473   | 1   |
| AE                   | 70.5           | 1   | 70.5        | 15.87   | 0       | 1   |
| BC                   | 4.3            | 1   | 4.3         | 0.96    | 0.33    | 1   |
| BD                   | 3.3            | 1   | 3.3         | 0.74    | 0.393   | 1   |
| BE                   | 1.3            | 1   | 1.3         | 0.29    | 0.59    | 1   |
| CD                   | 3035.8         | 1   | 3035.8      | 682.78  | 0       | 1   |
| CE                   | 24264          | 1   | 24264       | 5457.16 | 0       | 1   |
| DE                   | 2879.9         | 1   | 2879.9      | 647.71  | 0       | 1   |
| ABC                  | 0              | 1   | 0           | 0       | 0.992   | 1   |
| ABD                  | 0.2            | 1   | 0.2         | 0.06    | 0.814   | 1   |
| ABE                  | 0              | 1   | 0           | 0       | 0.957   | 1   |
| ACD                  | 57.3           | 1   | 57.3        | 12.89   | 0.001   | 1   |
| ACE                  | 60.5           | 1   | 60.5        | 13.6    | 0       | 1   |
| ADE                  | 3.4            | 1   | 3.4         | 0.76    | 0.388   | 1   |
| BCD                  | 0.3            | 1   | 0.3         | 0.08    | 0.782   | 1   |
| BCE                  | 1.6            | 1   | 1.6         | 0.36    | 0.549   | 1   |
| BDE                  | 0.5            | 1   | 0.5         | 0.11    | 0.744   | 1   |
| CDE                  | 232.7          | 1   | 232.7       | 52.33   | 0       | 1   |
| Error                | 311.2          | 64  |             |         |         |     |
| Total                | 95249.4        | 95  |             |         |         |     |
| $R^2$                |                |     | 99.67%      |         |         |     |
| Adjusted $R^2$       |                |     | 99.56%      |         |         |     |
| Predicted $R^2$      |                |     | 99.39%      |         |         |     |

An empirical model is presented in coded format to predict Glass Transition Temperature ( $T_g$ ) based on the statistical analysis of test data. Response equation based on coded factors allows the prediction of response by assigning +1/−1 levels to each independent process variable. In this study, the coded response is given by,

$$\begin{aligned} \text{Glass Transition Temperature } T_g [^{\circ}\text{F}] = & 263.516 + 0.350 P - 0.202 R_p + 21.290 T - 5.089 \\ & R_t + 13.664 t + 0.150 P R_p - 1.986 P T - 0.155 P R_t - 0.857 P t - 0.211 R_p T - 0.185 R_p R_t - \\ & 0.117 R_p t + 5.623 T R_t - 15.898 T t + 5.477 R_t t - 0.002 P R_p T - 0.051 P R_p R_t - 0.012 P \\ & R_p t - 0.773 P T R_t + 0.794 P T t - 0.187 P R_t t - 0.060 R_p T R_t - 0.129 R_p T t + 0.071 R_p R_t \\ & t - 1.557 T R_t t \end{aligned} \quad (3)$$

Equation (3) gives the statistical prediction of the  $T_g [^{\circ}\text{F}]$  of AF163-2K epoxy film adhesive. From Figure 3.21 (a) can be observed that residuals follow a normal distribution, as a straight line is fitted through the normal plot of residuals. Figure 3.21 (b) is a plot of the residuals versus the experimental run order, checks lurking variables that may have influenced the response during the analysis. Random scatter must be obvious; blocking and randomization of testing would minimize the probability of trends that may invalidate the analysis. Figure 3.22 shows single-variable effect on glass transition temperature  $T_g [^{\circ}\text{F}]$ . Lines with positive slopes indicates that increasing that factor would increase joint shear strength; the opposite is true as well. The value of the slope is a measure of how significant the factor is [23].

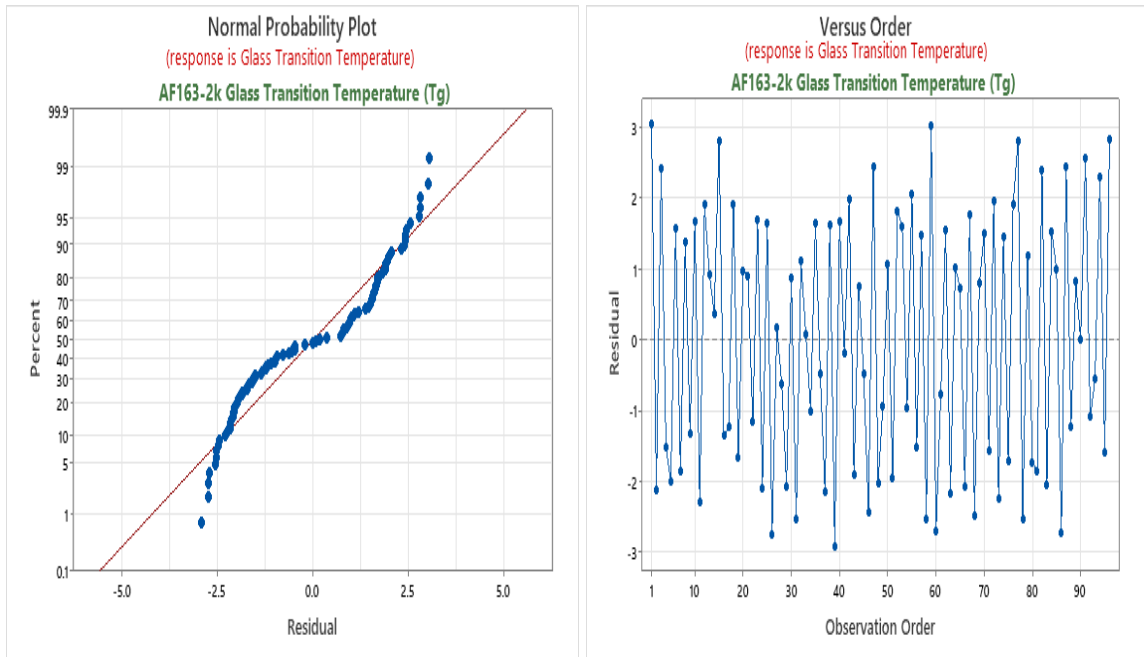


Figure 3.21 Glass Transition Temperature  
(a) Normal Plot of residuals (b) Residual vs. Run

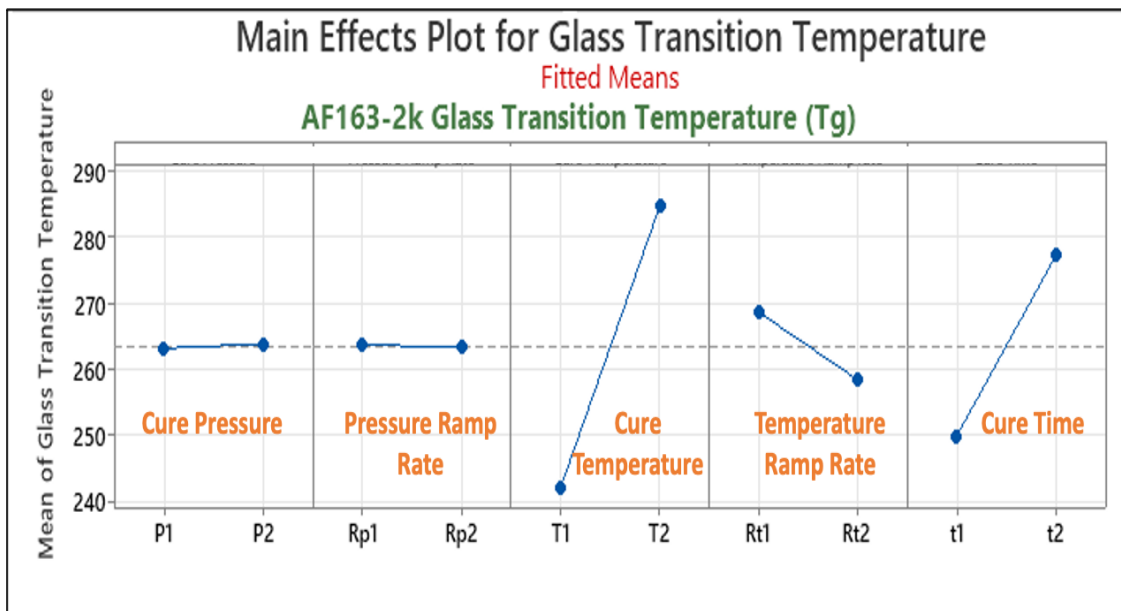


Figure 3.22 Single Variable Effect on Glass Transition Temperature (Tg)

## CHAPTER FOUR

### ALUMINUM BONDED JOINT WITH EPOXY ADHESIVE

#### 4.1 Introduction

Aluminum usage in automotive applications has grown more than 80% in the past 5 years. A total of about 110 kg of aluminum/vehicle in 1996 is predicted to rise to 400 or 440 kg, with or without taking body panel or structure applications into account, by 2025. There are strong predictions for aluminum application in hoods, trunk lids and doors hanging on a steel frame.

#### 4.2 Materials

Aluminum 6061 and Epoxy film adhesive AF163-2K from 3M are used; mechanical and thermal properties are shown in Table 4.1. Aluminum 6061 surface is coated with Electroless Nickel Plating Coatings Endura 200 prior bonding.

Table 4.1 Adherend Mechanical Properties

| Property         | Unit | Value |
|------------------|------|-------|
| Tensile strength | MPa  | 310   |
| Yield strength   | MPa  | 276   |
| Shear strength   | MPa  | 207   |
| Fatigue strength | MPa  | 96.5  |
| Elastic modulus  | GPa  | 68.9  |
| Poisson's ratio  | MPa  | 0.33  |



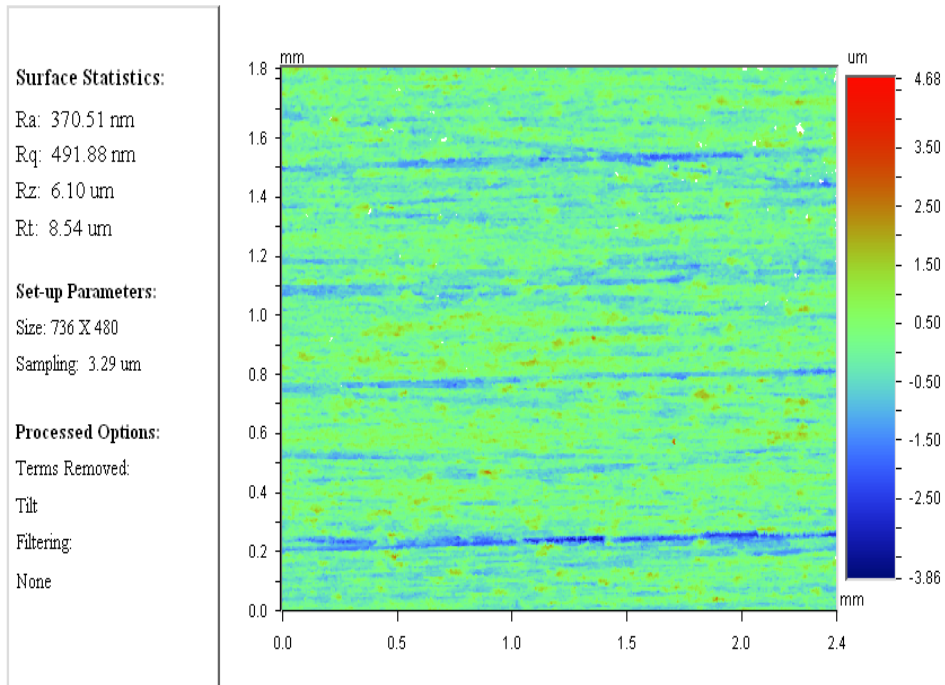
Mag: 2.6 X

Mode: VSI

## Surface Data

Date: 04/02/2019

Time: 11:12:21



Title:

Note:

Figure 4.1 3D Surface Roughness Inspection Image Data with Ra = 370.51 Nm

### 4.3 Joining Procedure

Aluminum adherends are bonded together using epoxy AF163-2K film adhesive using autoclave minibonder. Film adhesive is cut in the 1" X 1" pieces and placed in between two aluminum adherends. This loosely assembled joint was placed in vacuum bag with support plate to avoid bending of coupon during curing process.

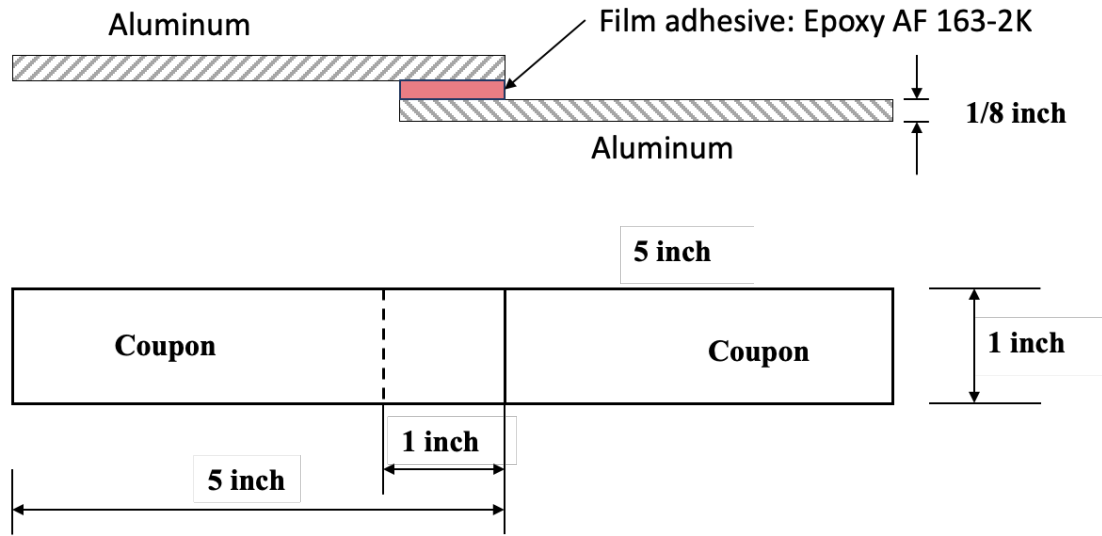


Figure 4.2 Aluminum SLJ Illustration

#### 4.4 Experimental Procedure and Test Setup

Aluminum SLJ from 32 different combinations of autoclave processes variables were tested in tensile shear for load transfer capacity (LTC) at ambient conditions to establish baseline results. Afterwards, the effect of environmental load was investigated with cyclic heat and high relative humidity conditions. Six test coupons were autoclave bonded for each 32- autoclave bonding process. From which three polycarbonate coupons were tested for baseline LTC at ambient conditions and three polycarbonate coupons were tested after cyclic heat at high relative humidity (RH) of 85%. Average test data is reported.

Static LTC of polycarbonate coupons was evaluated using MTS 810 Material Testing System, shown in Figure 4.3 Al-SLJ was held inside specially designed fixture and gripped vertically on MTS system. A quasi-static axial load is applied to the SLJ at a

constant speed of 1.27 mm/min. Displacement and forces are recorded by MTS data acquisition system. Failure modes have been documented for all test SLJs.

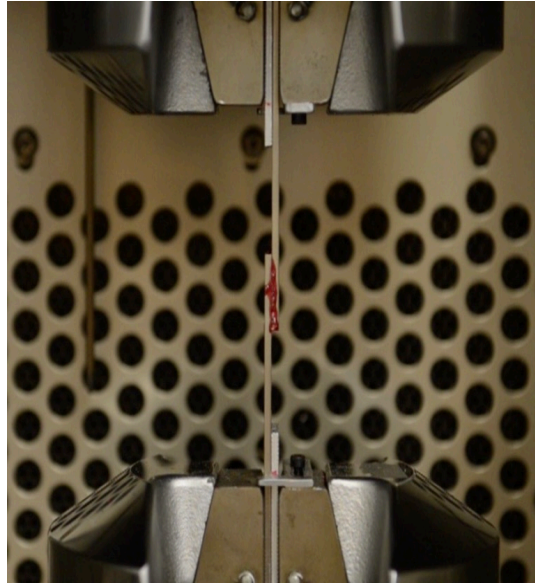


Figure 4.3 Static LTC Test Setup for Aluminum Joints

## 4.5 Result and Discussion

### 4.5.1 Baseline Static Load Transfer Capacity (LTC)

In this section experimental results are presented and discussed. Figure 4.4 gives comparative overview of static performance LTC and glass transition temperature ( $T_g$ ) of 32 autoclave processes designed with all possible combination of five process variables. Trendline for LTC and  $T_g$  follow each other very closely, depicting strong dependence of LTC on  $T_g$  of epoxy film adhesive cured with set of cure process variables. Baseline static LTC is higher for all autoclave process when compared to static LTC after cyclic

heat at high relative humidity. Higher baseline static LTC of 12929 N was observed autoclave process variables of cure temperature  $T_2 = 260$  °F, cure pressure  $P_2 = 100$  Psi, temperature ramp rate  $R_{t1} = 2$  °F/min, pressure ramp rate  $R_{p1} = 10$  Psi/min, cure time  $t_1 = 40$  min. Lower baseline static LTC 7208 kN was observed autoclave process variables of cure temperature  $T_1 = 200$  °F, cure pressure  $P_1 = 50$  Psi, temperature ramp rate  $R_{t2} = 7$  °F/min, pressure ramp rate  $R_{p1} = 10$  Psi/min, cure time  $t_1 = 40$  min. Baseline static LTC reduced after cyclic heat at high relative. Higher percentage reduction in LTC observed for autoclave processes with low cure temperature than high cure temperature. Highest reduction of 58% observed for autoclave process ID 10 with cure temperature  $T_1 = 200$  °F, cure pressure  $P_2 = 100$  Psi, temperature ramp rate  $R_{t2} = 7$  °F/min, pressure ramp rate  $R_{p1} = 10$  Psi/min, cure time  $t_1 = 40$  min. Lowest LTC reduction of 9% observed for autoclave process ID 22 with cure temperature  $T_2 = 260$  °F, cure pressure  $P_2 = 100$  Psi, temperature ramp rate  $R_{t1} = 2$  °F/min, pressure ramp rate  $R_{p1} = 10$  Psi/min, cure time  $t_2 = 90$  min.

Highest glass transition temperature ( $T_g$ ) of 306.2 °F was observed autoclave process variables of cure temperature  $T_2 = 260$  °F, cure pressure  $P_2 = 100$  Psi, temperature ramp rate  $R_{t1} = 2$  °F/min, pressure ramp rate  $R_{p2} = 15$  Psi/min, cure time  $t_1 = 40$  min. Lower glass transition temperature ( $T_g$ ) 197.2 °F was observed autoclave process variables of cure temperature  $T_1 = 200$  °F, cure pressure  $P_1 = 50$  Psi, temperature ramp rate  $R_{t2} = 7$  °F/min, pressure ramp rate  $R_{p2} = 15$  Psi/min, cure time  $t_1 = 40$  min. AF163-2K epoxy film adhesive and SLJ cured at low cure temperature ( $T_1$ ) have significant variation in Static LTC and glass transition temperature ( $T_g$ ) with change in cure process parameter as compared to those cured at high cure temperature ( $T_2$ ).

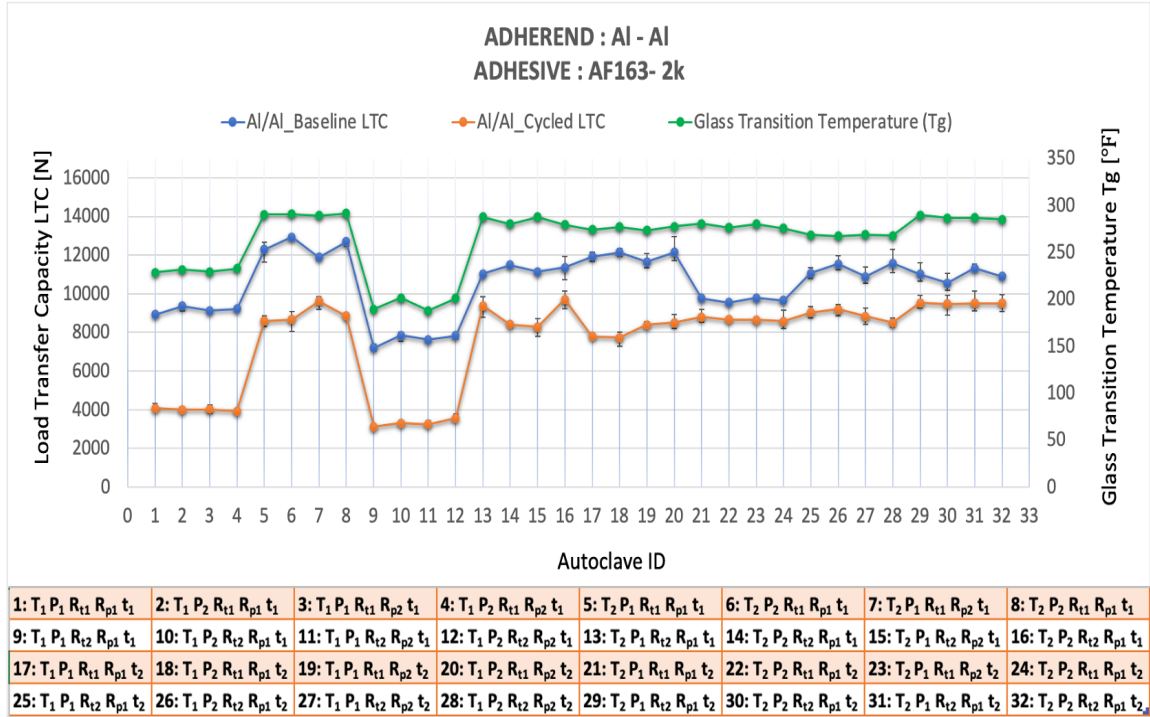


Figure 4.4 Combined plot for load transfer capacity (LTC) of Aluminum joints

Figure 4.5 shows baseline static performance of Al/Al SLJ is higher for high cure temperature ( $T_2 = 260^\circ\text{F}$ ) when compared to low cure temperature ( $T_1 = 200^\circ\text{F}$ ) for all low cure time ( $t_1$ ) processes when other variables ( $P$ ,  $R_t$ ,  $R_p$ ) remained same. Trend reverse for high cure time ( $t_2$ ) process where static LTC is higher or almost same for low cure temperature ( $T_1 = 200^\circ\text{F}$ ) as compared to high cure temperature ( $T_2 = 260^\circ\text{F}$ ). With increase in cure temperature glass transition temperature continue to rise to certain limit above vitrification until AF163-2K attain full curing and a decrease the free volume. Beyond the increase in cure temperature or cure time results in thermal degradation of polymeric chains which have negative effect on the static performance of epoxy film adhesive joints.

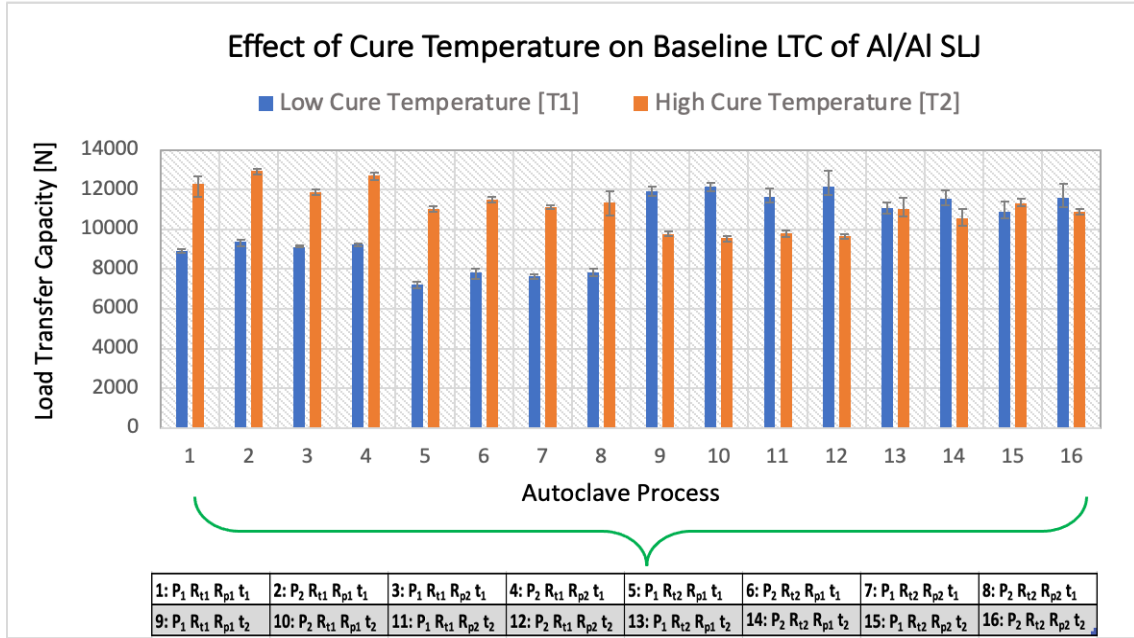


Figure 4.5 Effect of Cure Temperature on Baseline LTC of AL-SLJ with Epoxy Adhesive AF163-2K

Figure 4.6 shows effect of temperature ramp rate on baseline static LTC at room conditions when other process variables remained same ( $T$ ,  $R_t$ ,  $R_p$ ,  $t$ ). It shows lower temperature ramp rate ( $R_{t1}$ ) have positive effect on the LTC as compared with high cure temperature ( $R_t$ ), except for cure processes in combination with high cure temperature, high cure time ( $T_2$ ,  $R_{t1}$ ,  $t_2$ ). Low temperature ramp rate ensures longer cure process and more time for chemical reaction to form 3D cross linking of epoxy chains. Beyond vitrification the reaction rate epoxy system is governed by dispersion of physical monomers to form long chains. This slows down formation of 3D cross linking. More cure process time ensures more mobility of monomers to increase cross linking and degree of cure [21].

Figure 4.7 shows effect of cure pressure on static LTC when other process variables remained same ( $T$ ,  $P$ ,  $R_p$ ,  $t$ ). It is observed that high cure pressure results into higher static LTC when compared to low cure pressure, except for cure processes in combination with high cure temperature, high cure time ( $T_2$ ,  $P_2$ ,  $t_2$ ). High cure pressure results in formation of intermolecular hydrogen bonding between hydroxy groups and carbonyl groups also increased the interaction of the polymer chains. As a result, the free volume of the polymer decreased, and the polymer chains were packed more closely with the increased curing pressure. In summary, the increasing curing pressure moderately improve the cross-linking densities and the mechanical properties of the cured adhesive [22].

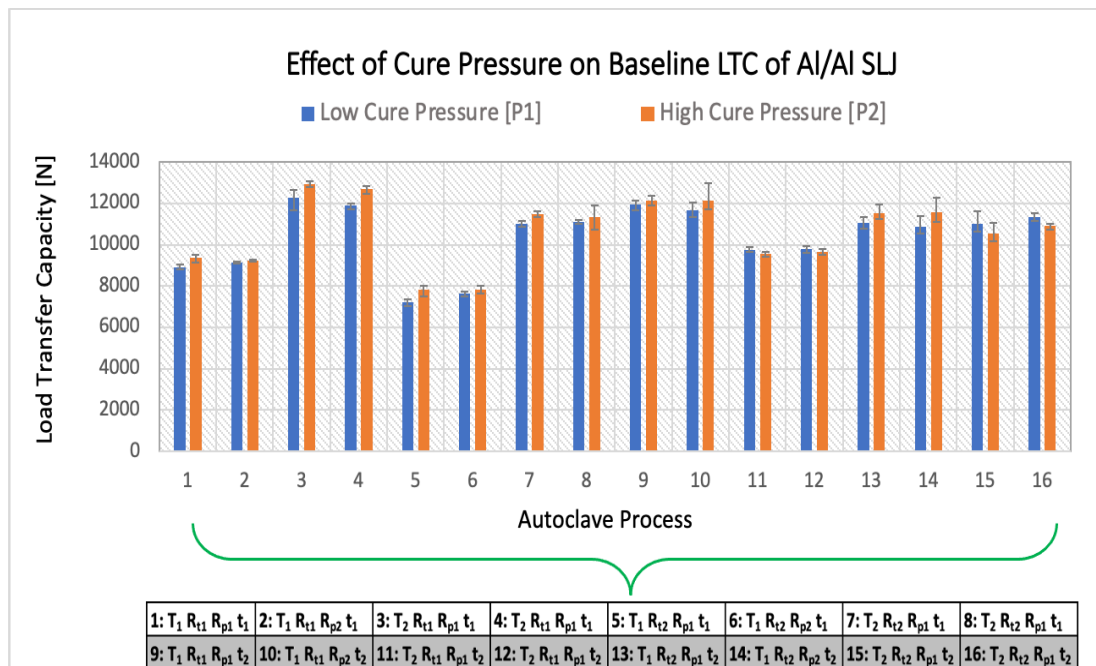


Figure 4.6 Effect of Cure Pressure on Baseline LTC of AL-SLJ with Epoxy Adhesive AF163-2K

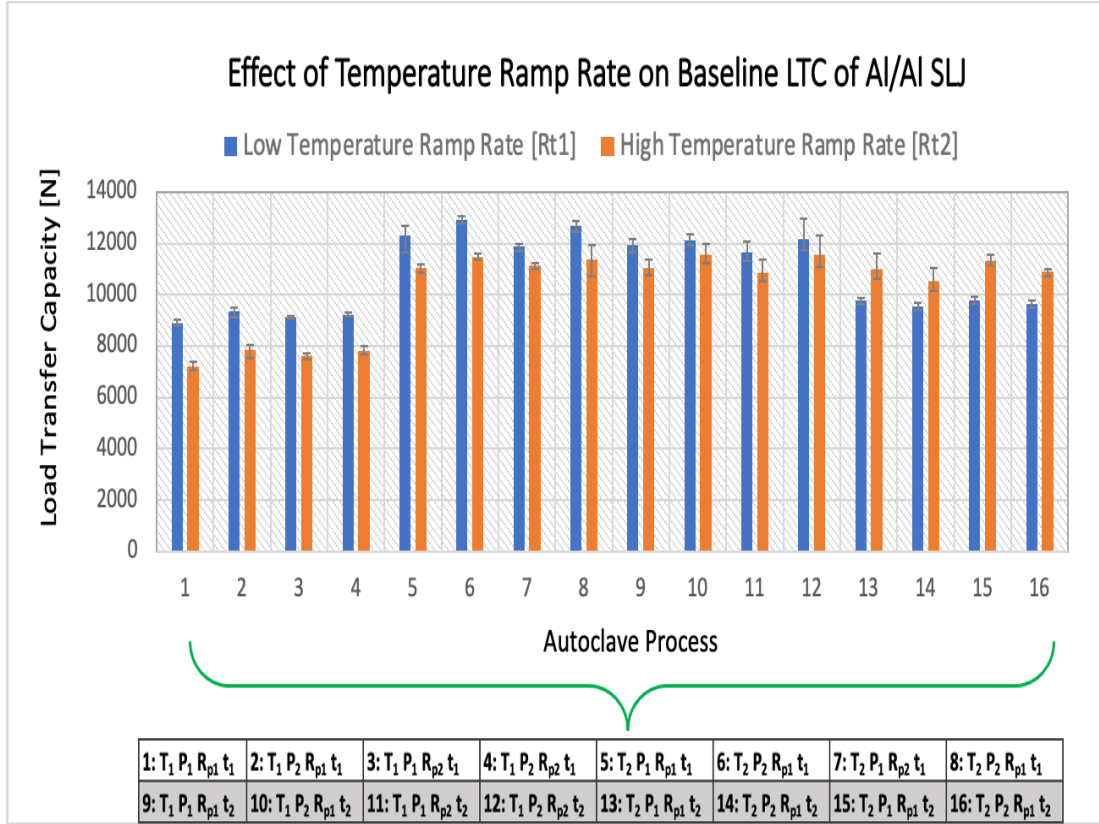


Figure 4.7 Effect of Temperature Ramp Rate on Baseline LTC of AL-SLJ with Epoxy Adhesive AF163-2K

Figure 4.8 shows effect of cure time on baseline static LTC, when other process variables remained same ( $P$ ,  $T$ ,  $R_t$ ,  $R_p$ ). It is observed that for most of autoclave processes, high cure time ( $t_2 = 100$  min) combined with low cure temperature ( $T_1 = 200$  °F) increased static performance of SLJ. Static LTC was lower for the high cure time process in combination with high cure temperature and low temperature ramp rate. The thermal degradation or oxidative crosslinking (above the  $T_{g\infty}$  of the adhesive) is held responsible for the decrease of strength with increasing curing time [21].



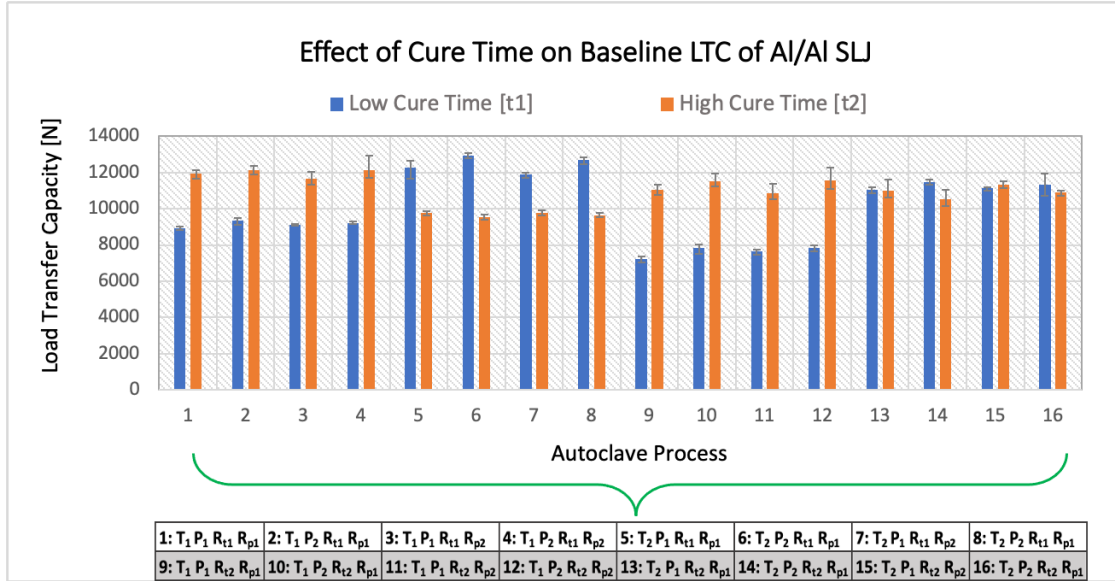


Figure 4.8 Effect of Cure Time on Baseline LTC of AL-SLJ with Epoxy Adhesive AF163-2K

#### 4.5.2 Environmental Cycling

From the visual inspection of Al – SLJ's, it is observed that cure temperature ( $T$ ) is most significant factor in the diffusion of moisture inside adhesive layer. Coupons that autoclave bonded with low cure temperature ( $T_1$ ) showed have lowered static performance after heat cycling at high relative humidity of 85% when compared to those bonded at high cure temperature ( $T_2$ ). Low cure temperature ( $T_1$ ) in combination with low cure time ( $t_1$ ) (Autoclave ID 1-4 ,9-12) were more susceptible to moisture diffusion than its combination with high cure time ( $t_2$ ) (Autoclave ID 17-20 ,25-28). Whereas High cure temperature, high cure time ( $t_2$ ) in combination with low pressure ramp rate ( $R_{p1}$ ) (Autoclave ID 21,22,29,30) have better resistance to moisture diffusion. Failure modes are shown in 4.9, for all Al-SLJ's failure cohesive starting from the edges and shear in the middle of joint.

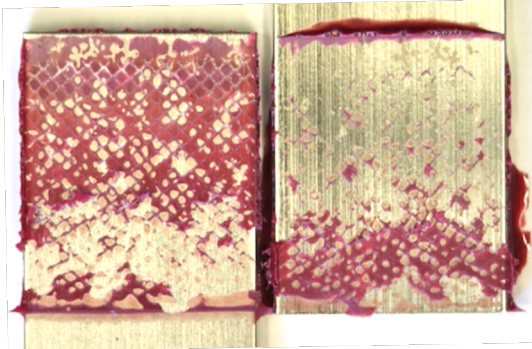
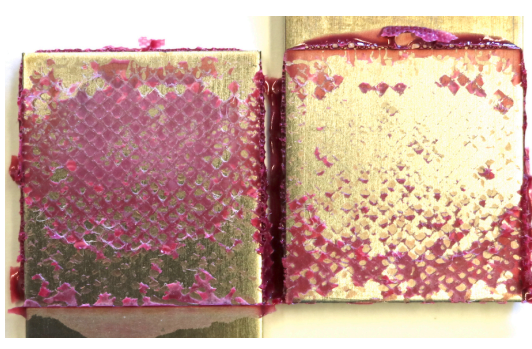
|       | At Baseline                                                                       | After Heat Cycling at 85% RH                                                       |
|-------|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------|
| Al/Al |  |  |

Figure 4.9 Failure modes in Al SLJ's

#### 4.6 ANOVA

Based on ANOVA data in Table 4.2, the cure pressure (A), cure temperature (c), temperature ramp rate (D), cure time (E) and their interactions are found to be significant as P-value is less than 0.05 for 95% confidence. Normal chart (Figure 4.10) shows the same significance of same factors and interactions.

The R-Squared shows how accurate the model is predicting the response values or the measurement of the amount of variation around the mean; R-Squared value that is closer to 1.0 is desirable. In this analysis, the value is equal to 0.9719, which is still acceptable. Additionally, the difference between Predicted  $R^2$  of 0.9369 and Adjusted  $R^2$  of 0.9583 is less than 0.2 which is favorable.

Table 4.2 ANOVA Data for Shear Strength of Baseline LTC of AL-SLJ's

| Source                   | Sum of Squares | dof | Mean Square | F-value | p-value | VIF |
|--------------------------|----------------|-----|-------------|---------|---------|-----|
| Model                    | 94938.1        | 25  | 3797.5      | 854.09  | 0       |     |
| Cure Pressure [A]        | 11.7           | 1   | 11.7        | 2.64    | 0.109   | 1   |
| Press. Ramp Rate [B]     | 3.9            | 1   | 3.9         | 0.88    | 0.35    | 1   |
| Cure Temperature [C]     | 43514.1        | 1   | 43514.1     | 9786.65 | 0       | 1   |
| Temp. Ramp Rate [D]      | 2486.2         | 1   | 2486.2      | 559.17  | 0       | 1   |
| Cure time [E]            | 17923.5        | 1   | 17923.5     | 4031.14 | 0       | 1   |
| AB                       | 2.2            | 1   | 2.2         | 0.49    | 0.488   | 1   |
| AC                       | 378.5          | 1   | 378.5       | 85.14   | 0       | 1   |
| AD                       | 2.3            | 1   | 2.3         | 0.52    | 0.473   | 1   |
| AE                       | 70.5           | 1   | 70.5        | 15.87   | 0       | 1   |
| BC                       | 4.3            | 1   | 4.3         | 0.96    | 0.33    | 1   |
| BD                       | 3.3            | 1   | 3.3         | 0.74    | 0.393   | 1   |
| BE                       | 1.3            | 1   | 1.3         | 0.29    | 0.59    | 1   |
| CD                       | 3035.8         | 1   | 3035.8      | 682.78  | 0       | 1   |
| CE                       | 24264          | 1   | 24264       | 5457.16 | 0       | 1   |
| DE                       | 2879.9         | 1   | 2879.9      | 647.71  | 0       | 1   |
| ABC                      | 0              | 1   | 0           | 0       | 0.992   | 1   |
| ABD                      | 0.2            | 1   | 0.2         | 0.06    | 0.814   | 1   |
| ABE                      | 0              | 1   | 0           | 0       | 0.957   | 1   |
| ACD                      | 57.3           | 1   | 57.3        | 12.89   | 0.001   | 1   |
| ACE                      | 60.5           | 1   | 60.5        | 13.6    | 0       | 1   |
| ADE                      | 3.4            | 1   | 3.4         | 0.76    | 0.388   | 1   |
| BCD                      | 0.3            | 1   | 0.3         | 0.08    | 0.782   | 1   |
| BCE                      | 1.6            | 1   | 1.6         | 0.36    | 0.549   | 1   |
| BDE                      | 0.5            | 1   | 0.5         | 0.11    | 0.744   | 1   |
| CDE                      | 232.7          | 1   | 232.7       | 52.33   | 0       | 1   |
| Error                    | 311.2          | 64  |             |         |         |     |
| Total                    | 95249.4        | 95  |             |         |         |     |
| R <sup>2</sup>           |                |     | 97.19%      |         |         |     |
| Adjusted R <sup>2</sup>  |                |     | 95.83%      |         |         |     |
| Predicted R <sup>2</sup> |                |     | 93.69%      |         |         |     |

In addition, Variance Inflation Factor (VIF) with value of 1 indicates an ideal correlation between the regression coefficients or how much the variance around the estimated coefficient is inflated by the lack of orthogonality, in which all the model terms are orthogonal to all other factors in this study. VIFs values more than 10 would raise alarm that present coefficients are poorly estimated because of multi-co-linearity.

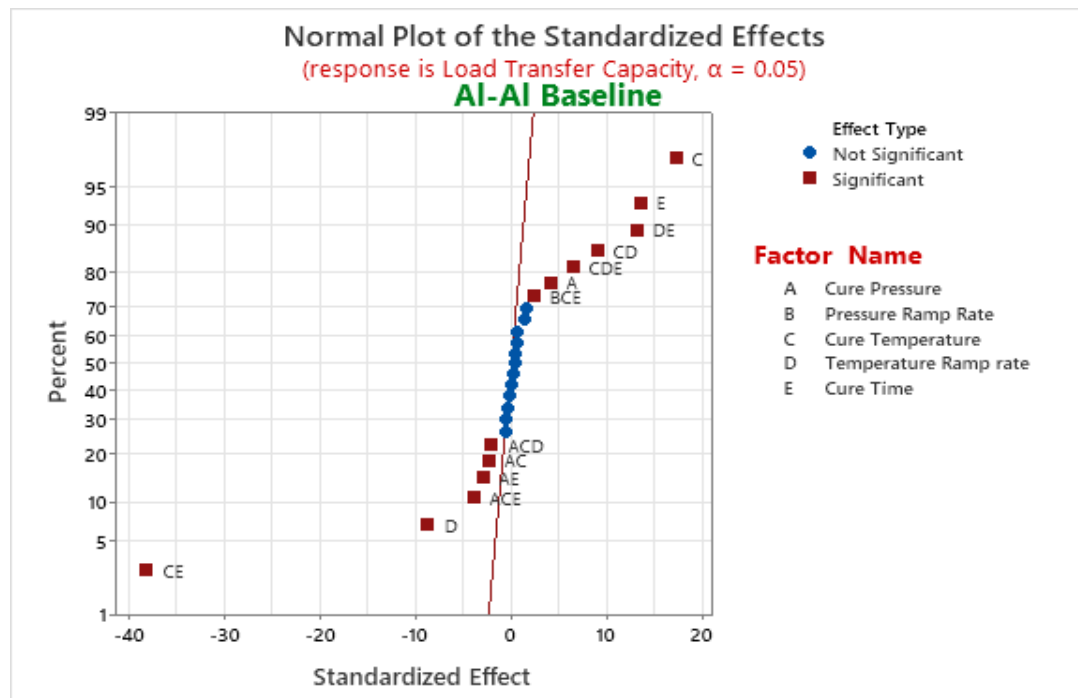


Figure 4.10 Normal Plot for Baseline Shear Strength of Al-SLJ's

An empirical model is presented in coded format to predict joint shear strength based on the statistical analysis of test data. Response equation based on coded factors

allows the prediction of response by assigning +1/-1 levels to each independent process variable. In this study, the coded response is given by,

$$\begin{aligned} \text{Al/Al Baseline LTC (N)} = & 9463.54 + 0.3645 P - 0.2082 R_p + 22.3541 T - 5.3439 R_t \\ & + 14.3436 t + 0.1603 P R_p - 2.0853 P T - 0.1666 P R_t - 0.8999 P t - 0.2209 R_p T - 0.1939 \\ & R_p R_t - 0.1189 R_p t + 5.9022 T R_t - 16.6895 T t + 5.7501 R_t t - 0.0020 P R_p T - 0.0499 P \\ & R_p R_t - 0.0124 P R_p t - 0.8126 P R_p t + 0.8332 P T R_t - 0.1939 P R_t t - 0.060 R_p T R_t \\ & - 0.1395 R_p T t + 0.0751 R_p R_t t - 1.6376 T R_t t \end{aligned} \quad (4)$$

Equation (4) gives the statistical prediction of the shear strength (N) of Baseline joints that have not been heat cycled. From Fig. 4.11 (a) can be observed that residuals follow a normal distribution, as a straight line is fitted through the normal plot of residuals. Figure 4.11 (b) is a plot of the residuals versus the experimental run order, checks lurking variables that may have influenced the response during the analysis. Random scatter must be obvious; blocking and randomization of testing would minimize the probability of trends that may invalidate the analysis. Fig. 4.12 shows single-variable effect on Baseline shear strength. Lines with positive slopes indicates that increasing that factor would increase joint shear strength; the opposite is true as well. The value of the slope is a measure of how significant the factor is [14].

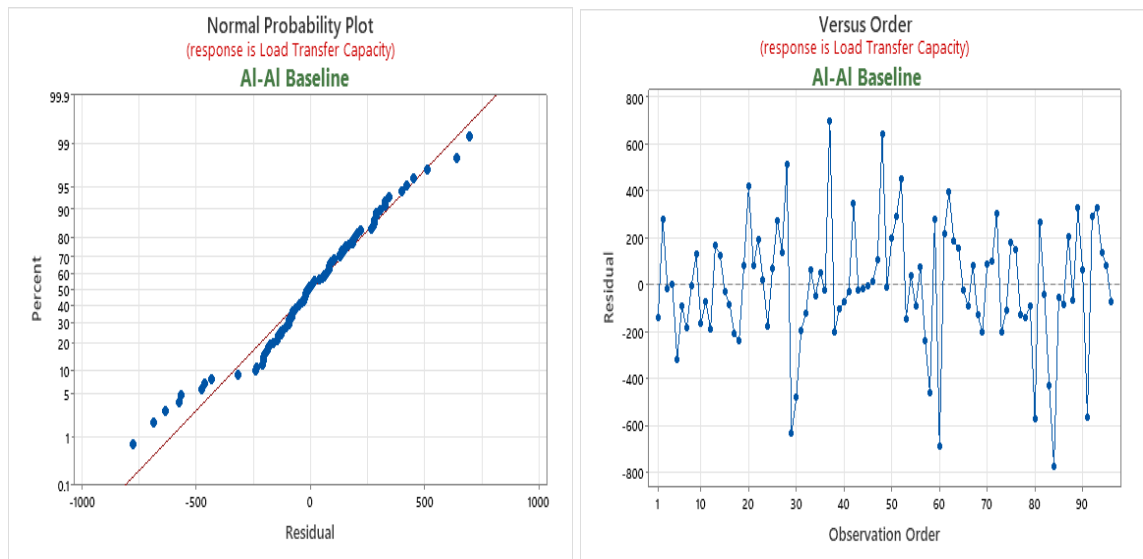


Figure 4.11 Baseline Static LTC of AI-SLJ's  
(a) Normal Plot of residuals (b) Residual vs. Run

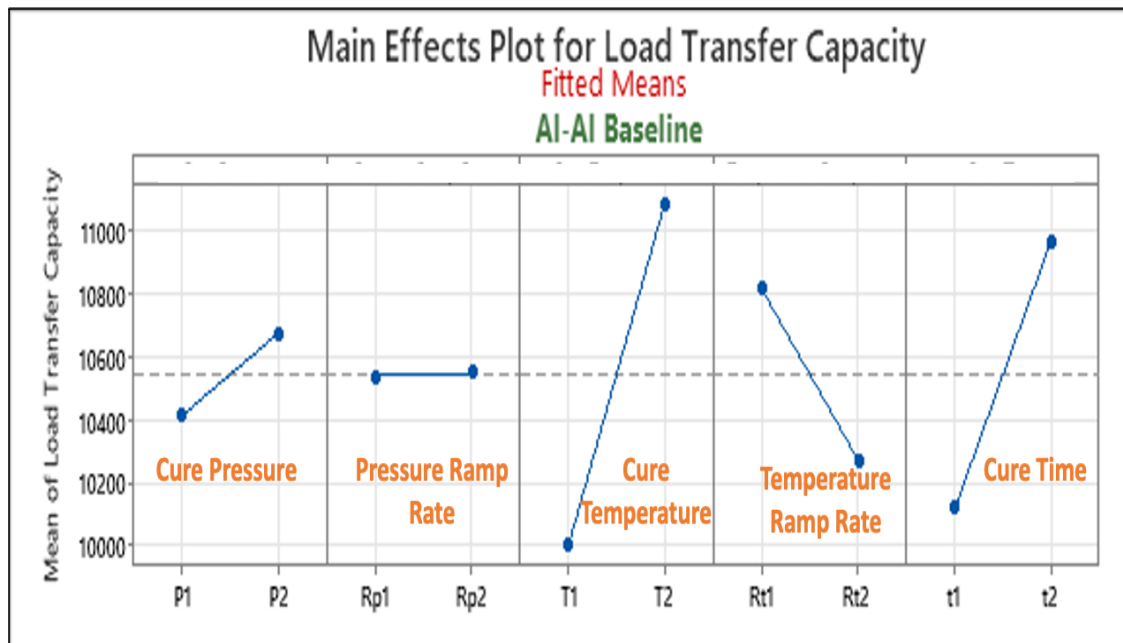


Figure 4.12. Single Variable Effect on baseline LTC of AI-SLJ's

## CHAPTER FIVE

### GRPF BONDED JOINT WITH EPOXY ADHESIVE

#### 5.1 Introduction

Fiber reinforced polymer (FRP) composites have found increasingly used in automotive and aircraft structures due to their advantageous properties, such as light weight, high tensile strength, dimensional stability, adequate electrical properties, and excellent corrosion resistance which make them attractive to the structural applications. Due to the increasing demand of high-performance materials in structural applications, fiber reinforced plastic (FRP) composites have gained much attention owing to their unique properties such as low density, high stiffness, high strength, and light weight.

#### 5.2 Materials

Extren 500 is fabricated with [0/90°] layup with E-type glass fibers in a Isophthalic polyester resin and filler of clay or calcium carbonate. GFRP material properties are shown in, Table 5.1. Epoxy AF163-2K film adhesive is used to bond two GFRP adherends in autoclave.

#### 5.3 Joining Procedure

Epoxy film adhesive AF 163-2K was cut into 1” x 1” pieces and placed in between GFRP adherend. The loose joint is then placed in a vacuum bag to be transferred into autoclave to begin curing process. GFRP test coupons from 32 different combinations of autoclave processes variables were tested in tensile shear for load transfer capacity (LTC) at ambient conditions to establish baseline results. Afterwards, the effect of environmental load was investigated with cyclic heat and high relative

humidity conditions. Six test coupons were autoclave bonded for each 32- autoclave bonding process. From which three polycarbonate coupons were tested for baseline LTC at ambient conditions and three polycarbonate coupons were tested after cyclic heat at high relative humidity (RH) of 85%. Average test data is reported.

Table 5.1 GFRP Adherend Mechanical Properties

| Property        | Unit                     | Value |
|-----------------|--------------------------|-------|
| Shear modulus   | GPa                      | 2.93  |
| Elastic modulus | GPa                      | 17.9  |
| Poisson's ratio |                          | 0.33  |
| Barcol Hardness |                          | 45    |
| Density         | $10^{-3} \text{ g/mm}^3$ | 1.8   |

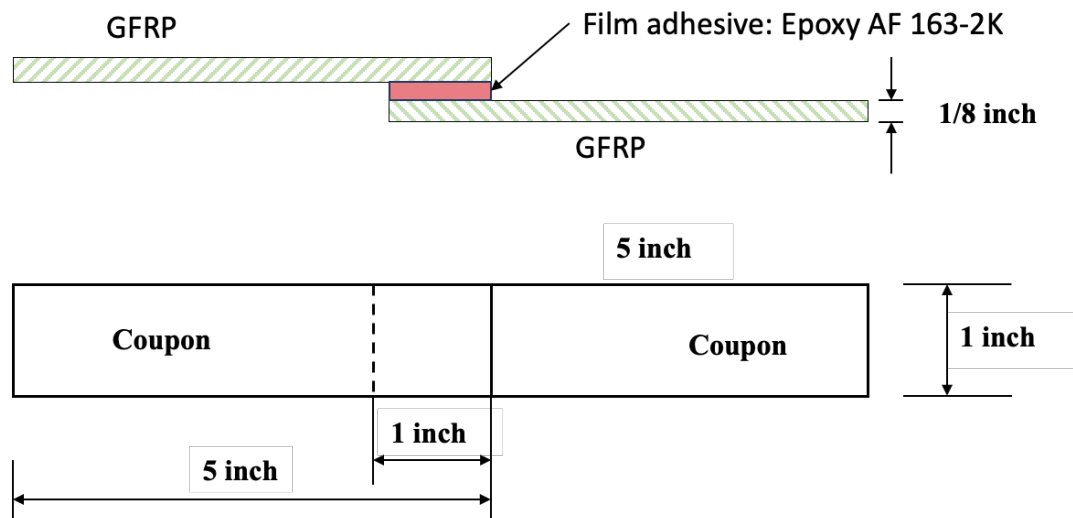


Figure 5.1 Illustration of GFRP Joint with Epoxy AF163-2K adhesive



## 5.4 Experimental Procedure and Test Setup

First, baseline static and dynamic testing is performed to establish the load transfer capacity of test joints at ambient environmental conditions for all combinations of coupon materials and joining methods. Subsequently, the effect of environmental load on the performance is investigated. Experimental data is generated from a sample size of all three replicas of each test; averages of three specimens from each test results are graphically tabulated.

### 5.4.1 Static Load Transfer Capacity (LTC) Testing

Static LTC of polycarbonate coupons was evaluated using MTS 810 Material Testing System, shown in Figure 5.2. Coupons were held inside specially designed fixture and gripped vertically on MTS system. A quasi-static axial load is applied to the coupon at a constant speed of 1.27 mm/min. Displacement and forces are recorded by MTS data acquisition system. Failure modes have been documented for all test coupons.

### 5.4.2 Static Load Transfer Capacity (LTC) Testing after Environmental Cycling

Single lap joint (SLJ) of GFRP-GFRP tested for cyclic heat at high relative humidity (RH) of 85%. Three SLJ coupons bonded from each of 32 different autoclave processes were transferred into an environmental chamber (Thermotron SE-300). The temperature cycles in the ranges of 20 – 75 °C for six 12-hours cycles following the profile.

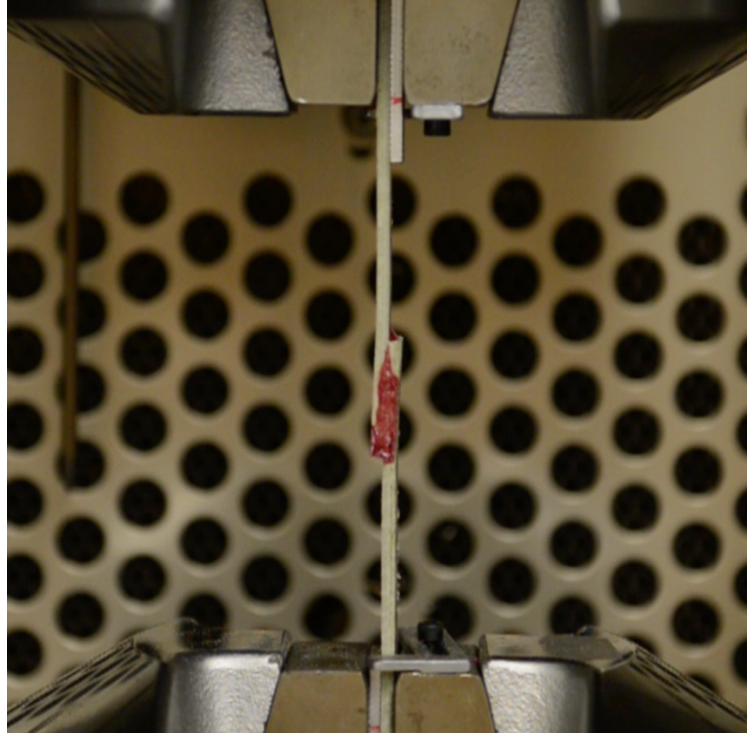


Figure 5.2 Static LTC Test Setup with GFRP SLJ

## 5.5 Results and Discussion

### 5.5.1 Baseline Static Load Transfer Capacity (LTC)

In this section experimental results are presented and discussed. Figure 5.3 gives comparative overview of static performance LTC and glass transition temperature ( $T_g$ ) of 32 autoclave processes designed with all possible combination of five process variables. Trendline for LTC and  $T_g$  follow each other very closely, depicting strong dependence of LTC on  $T_g$  of epoxy film adhesive cured with set of cure process variables. Higher baseline static LTC of 6512 N was observed autoclave process variables of cure temperature  $T_2 = 260$  °F, cure pressure  $P_1 = 50$  Psi, temperature ramp rate  $R_{t1} = 2$  °F/min,

pressure ramp rate  $R_{p1} = 10$  Psi/min, cure time  $t_2 = 100$  min. Lower baseline static LTC 3533.9 kN was observed autoclave process variables of cure temperature  $T_1 = 200$  °F, cure pressure  $P_2 = 100$  Psi, temperature ramp rate  $R_{t2} = 7$  °F/min, pressure ramp rate  $R_{p1} = 10$  Psi/min, cure time  $t_1 = 40$  min. Baseline static LTC reduced after cyclic heat at high relative. Higher percentage reduction in LTC observed for autoclave processes with low cure temperature than high cure temperature. Highest reduction of 52% observed for autoclave process ID 12 with cure temperature  $T_1 = 200$  °F, cure pressure  $P_2 = 100$  Psi, temperature ramp rate  $R_{t2} = 7$  °F/min, pressure ramp rate  $R_{p2} = 15$  Psi/min, cure time  $t_1 = 40$  min. Lowest LTC reduction of 3% observed for autoclave process ID 30 with cure temperature  $T_2 = 260$  °F, cure pressure  $P_2 = 100$  Psi, temperature ramp rate  $R_{t2} = 7$  °F/min, pressure ramp rate  $R_{p1} = 10$  Psi/min, cure time  $t_2 = 90$  min.

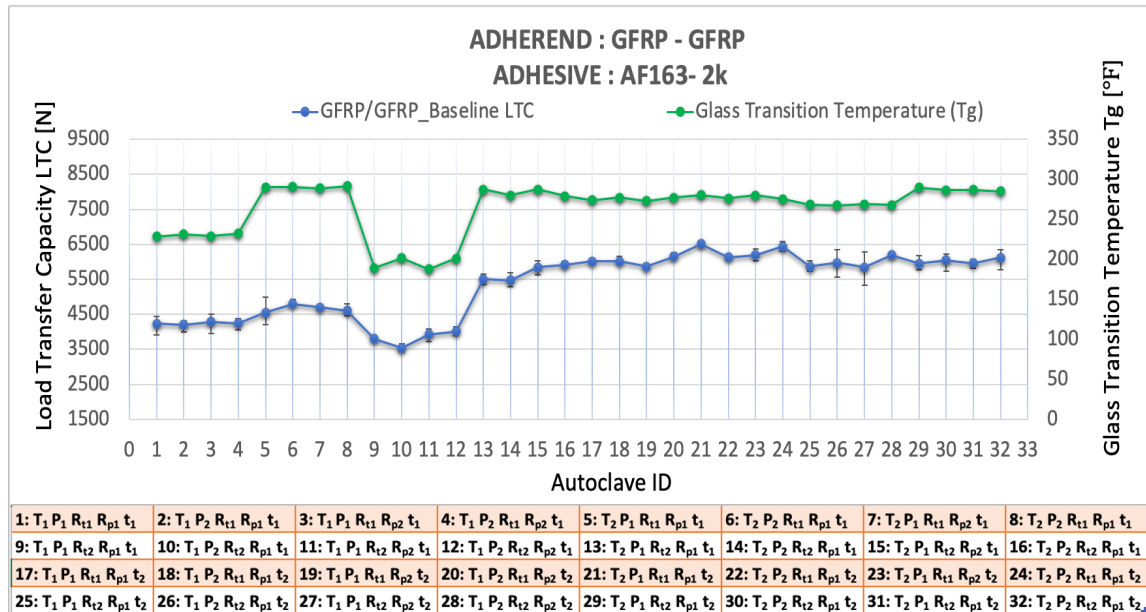


Figure 5.3 Combined plot for load transfer capacity (LTC) of GFRP joints

Figure 5.4 shows baseline static performance of GFRP SLJ's is higher for high cure temperature ( $T_2 = 260$  °F) when compared to low cure temperature ( $T_1 = 200$  °F) for all autoclave processes when other variables ( $P$ ,  $R_t$ ,  $R_p$ ,  $t$ ) remained same. Average static LTC for coupons bonded at high cure temperature is 5010.6 N, while those bonded at low cure temperature has 5673.3 N average LTC. Higher increase in LTC was observed for autoclave processes with cure pressure  $P_1 = 50$  Psi, temperature ramp rate  $R_{t2} = 7$  °F/min, pressure ramp rate  $R_{p2} = 15$  Psi/min, cure time  $t_2 = 90$  min, where LTC increased from 4210 N at low cure temperature to 6471 N at high cure temperature.

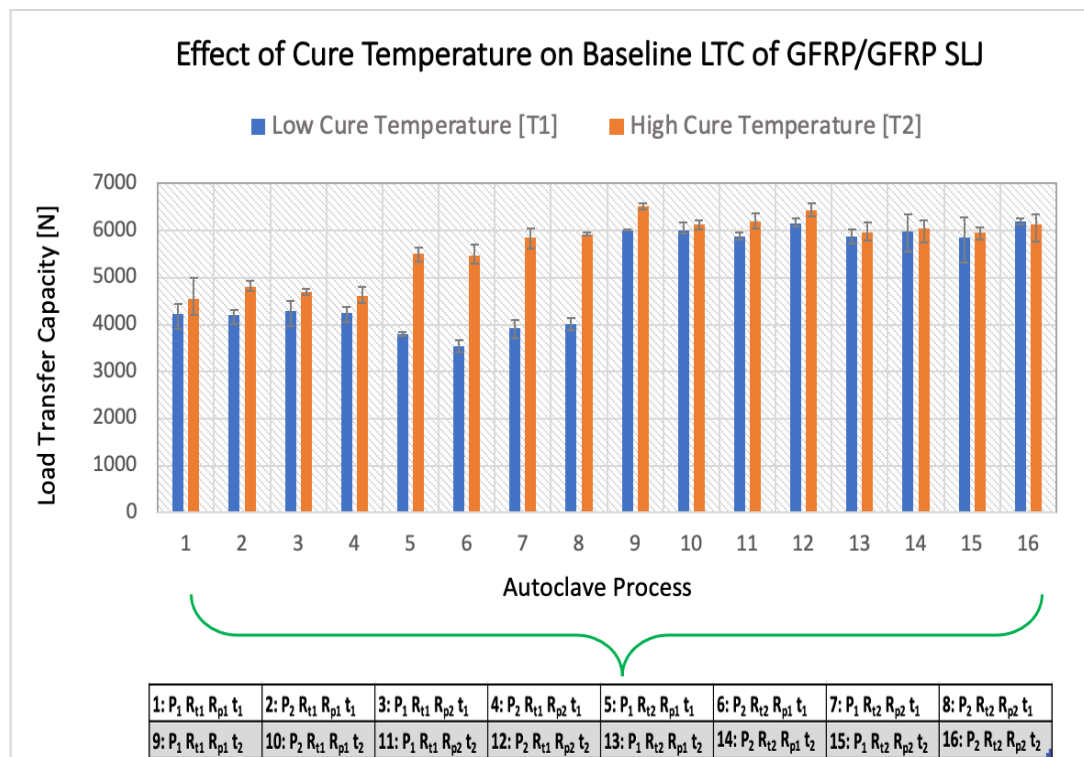


Figure 5.4 Effect of Cure Temperature on Baseline LTC of GFRP-SLJ with Epoxy Adhesive AF163-2K

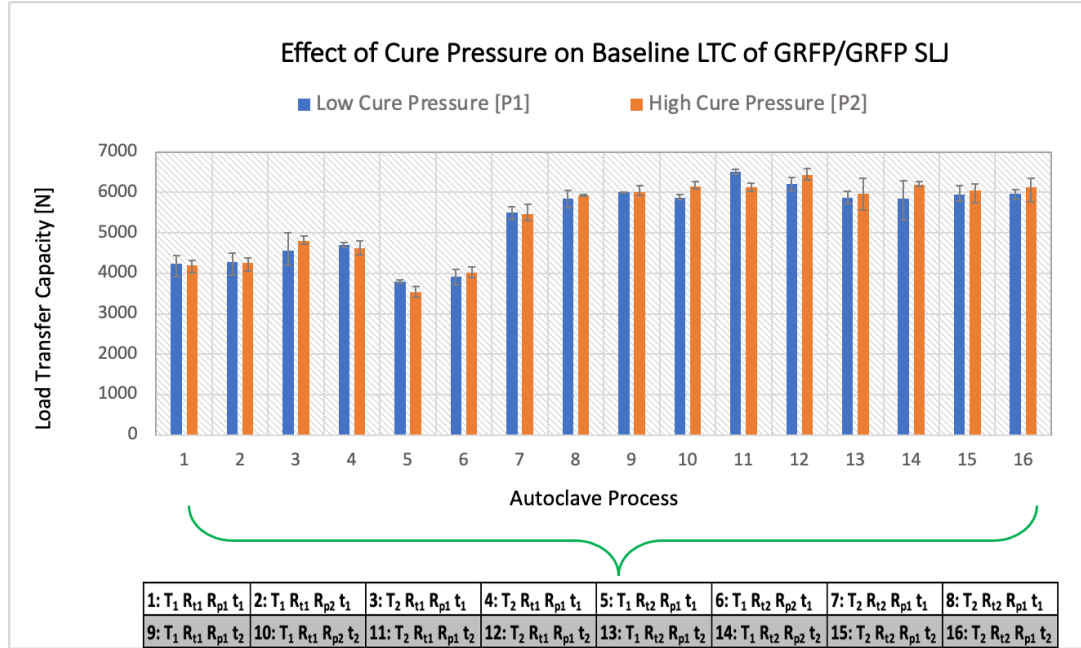


Figure 5.5 Effect of Cure Pressure on Baseline LTC of GFRP-SLJ with Epoxy Adhesive AF163-2K

Figure 5.5 shows effect of temperature ramp rate on static LTC when other process variables remained same ( $T$ ,  $P$ ,  $R_p$ ,  $t$ ). It is observed that high temperature ramp rate combined with high cure temperature always have higher static LTC when compared to low temperature ramp rate and its combination with high cure temperature. Average LTC for low temperature ramp rate and high temperature ramp rate was 5010.6 N and 5673.3 N respectively.

Figure 5.6 shows effect of cure pressure on baseline static LTC at room conditions when other process variables remained same ( $T$ ,  $R_t$ ,  $R_p$ ,  $t$ ). Average LTC for low cure pressure and high cure pressure was 5310 N and 5373 N. It is observed that effect of cure pressure alone on LTC is insignificant.

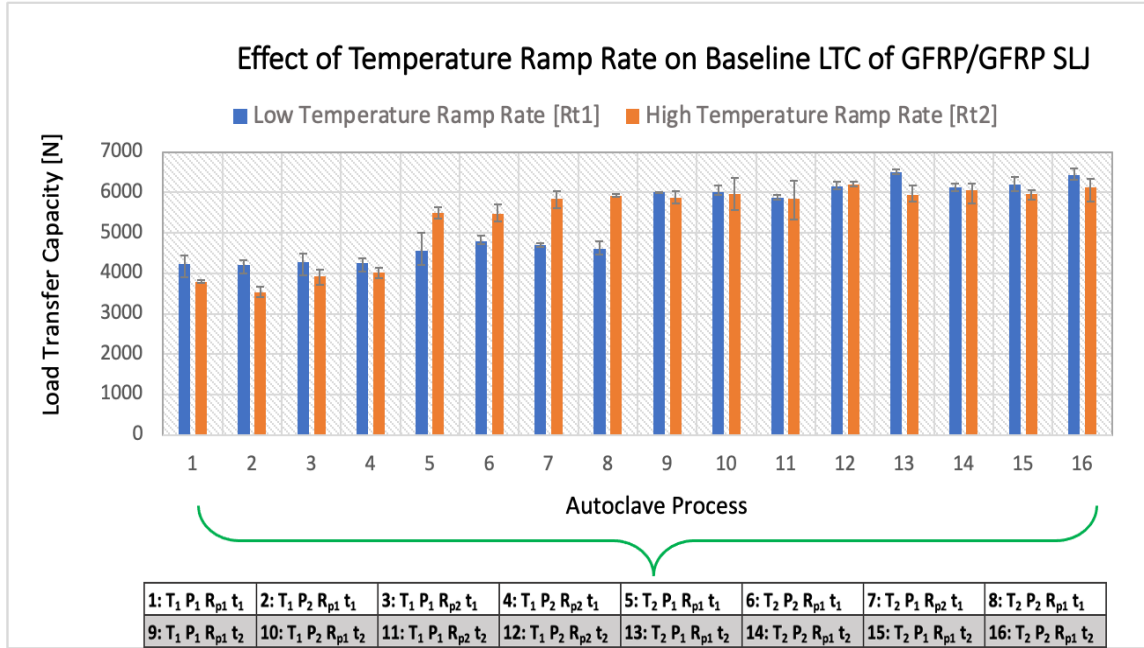


Figure 5.6 Effect of Temperature Ramp Rate on Baseline LTC of GFRP-SLJ with Epoxy Adhesive AF163-2K

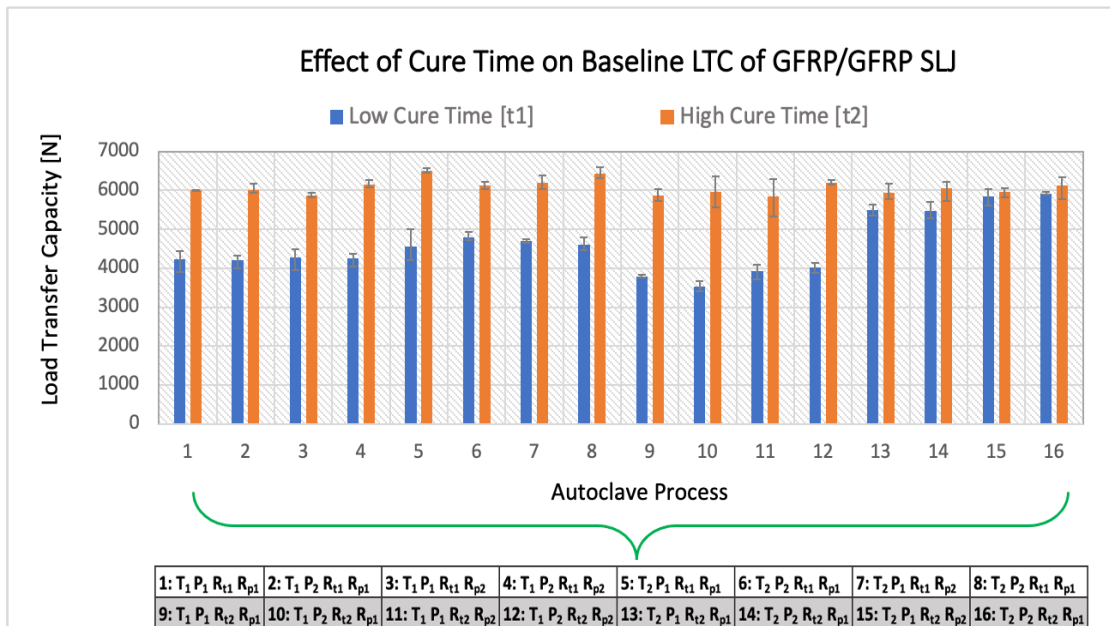


Figure 5.7 Effect of Cure Time on Baseline LTC of GFRP-SLJ with Epoxy Adhesive AF163-2K

Figure 5.7 shows effect of cure time on baseline static LTC, when other process variables remained same ( $P$ ,  $T$ ,  $R_t$ ,  $R_p$ ). It is observed that for most of autoclave processes, high soak time ( $t_2 = 100$  min) higher static performance of GFRP SLJ's. Average static LTC for low cure time and high cure time was 4602.7 N and 6081.1 N.

### 5.5.2 Environmental Cycling

Figure 5.8 and 5.9 presents visual appearance of polycarbonate coupon joint bonded at low/high cure temperature at ambient conditions and after environmental loading. Coupons that autoclave bonded with low cure temperature ( $T_1$ ) showed lower LTC after heat cycling at high relative humidity of 85% when compared to those bonded at high cure temperature ( $T_2$ ). Low cure temperature ( $T_1$ ) in combination with low cure time ( $t_1$ ) (Autoclave ID 1-4 ,9-12) were more susceptible to moisture diffusion than its combination with high cure time ( $t_2$ ) (Autoclave ID 17-20 ,25-28). Whereas High cure temperature, high cure time ( $t_2$ ) in combination with low pressure ramp rate ( $R_{p1}$ ) (Autoclave ID 21,22,29,30) have better resistance to moisture diffusion when compared to their combination with high pressure ramp rate ( $R_{p2}$ ) (Autoclave ID 23,24,31,32).

### 5.6 ANOVA

Based on ANOVA data in Table 5.2, the cure temperature (A), cure time (E), pressure ramp rate (B), interactions CD, CE, DE of cure temperature, temperature ramp rate and cure time are found to be significant as P-value is less than 0.05 for 95% confidence. Normal chart (Figure 5.11) shows the significance of same factors. The R-Squared shows how accurate the model is predicting the response values or the measurement of the amount of variation around the mean; R-Squared value that is closer to 1.0 is desirable. In this analysis, the value is equal to 0.9632, which is still acceptable.

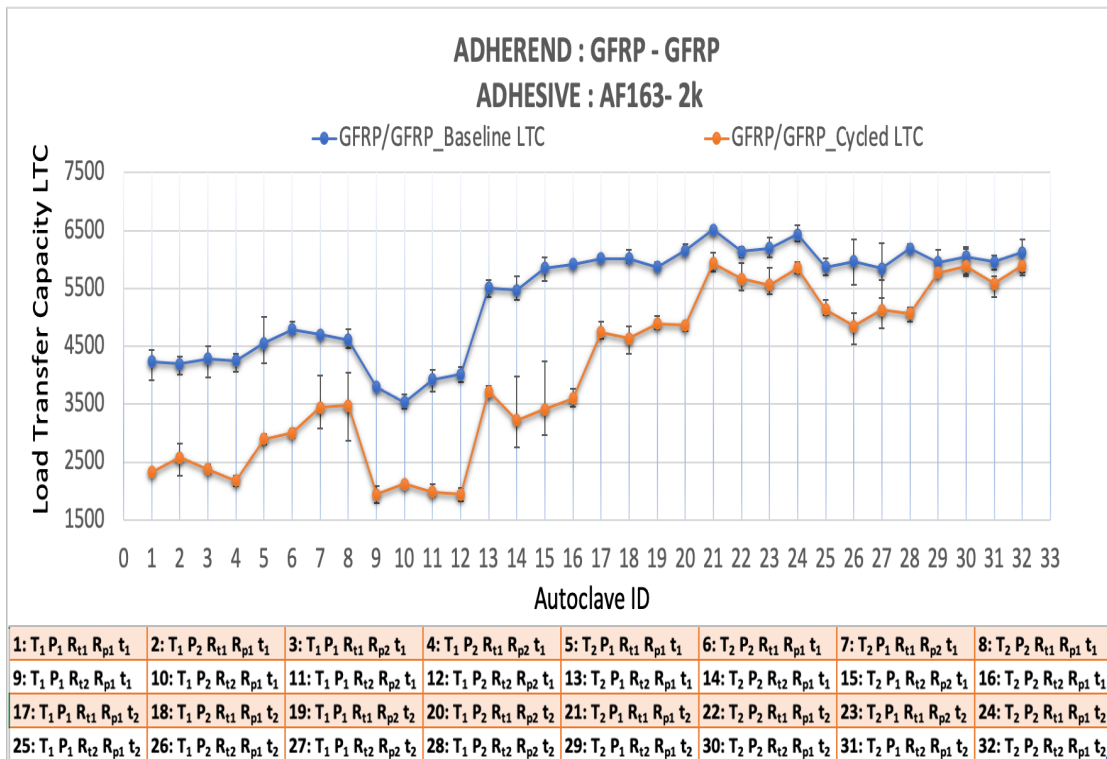


Figure 5.8 Effect of Environmental Loading on the LTC of GFRP Joints

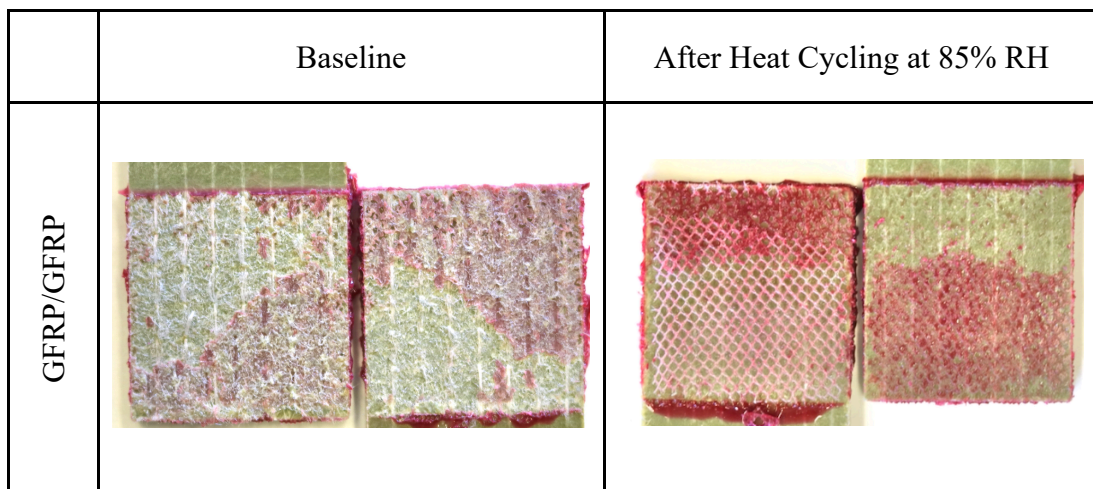


Figure 5.9 Failure modes in GFRP SLJ



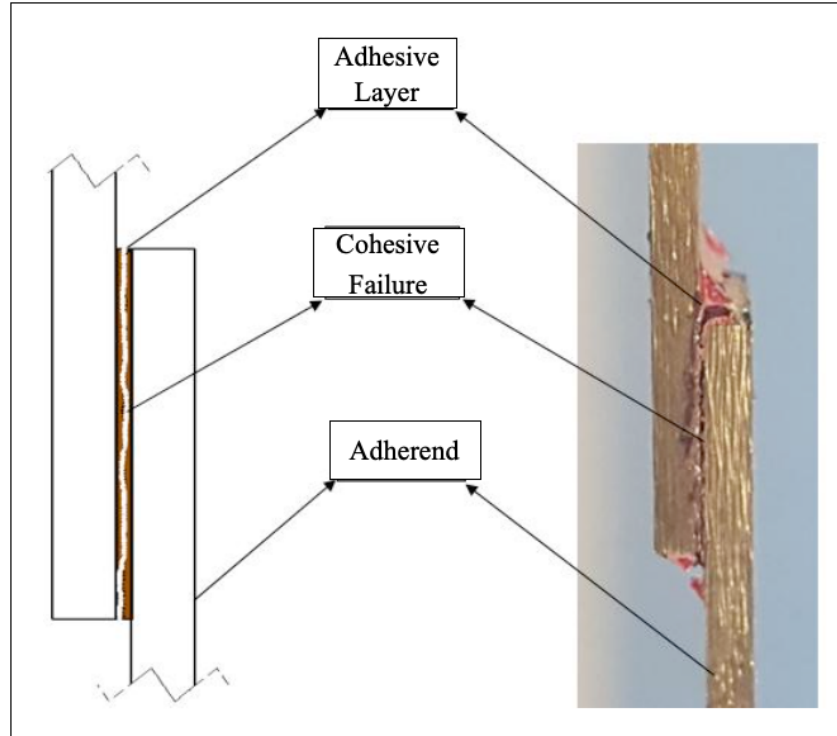


Figure 5.10 Cohesive Failure Mode in GFRP Joints

Additionally, the difference between Predicted  $R^2$  of 0.9307 and Adjusted  $R^2$  of 0.95 is less than 0.2 which is favorable.

In addition, Variance Inflation Factor (VIF) with value of 1 indicates an ideal correlation between the regression coefficients or how much the variance around the estimated coefficient is inflated by the lack of orthogonality, in which all the model terms are orthogonal to all other factors in this study. VIFs values more than 10 would raise alarm that present coefficients are poorly estimated because of multi-co-linearity.

Table 5.2 ANOVA Data for Baseline Static LTC of GFRP Joints

| Source                   | Sum of Squares | dof | Mean Square | F-value | p-value | VIF |
|--------------------------|----------------|-----|-------------|---------|---------|-----|
| Model                    | 77955503       | 25  | 3118220     | 73.22   | 0       |     |
| Cure Pressure [A]        | 61799          | 1   | 61799       | 1.45    | 0.232   | 1   |
| Press. Ramp Rate [B]     | 276532         | 1   | 276532      | 6.49    | 0.013   | 1   |
| Cure Temperature [C]     | 10499291       | 1   | 10499291    | 246.55  | 0       | 1   |
| Temp. Ramp Rate [D]      | 99721          | 1   | 99721       | 2.34    | 0.13    | 1   |
| Cure time [E]            | 52545840       | 1   | 52545840    | 1233.9  | 0       | 1   |
| AB                       | 172952         | 1   | 172952      | 4.06    | 0.048   | 1   |
| AC                       | 2792           | 1   | 2792        | 0.07    | 0.799   | 1   |
| AD                       | 9836           | 1   | 9836        | 0.23    | 0.632   | 1   |
| AE                       | 73387          | 1   | 73387       | 1.72    | 0.194   | 1   |
| BC                       | 1165           | 1   | 1165        | 0.03    | 0.869   | 1   |
| BD                       | 256720         | 1   | 256720      | 6.03    | 0.017   | 1   |
| BE                       | 127778         | 1   | 127778      | 3       | 0.088   | 1   |
| CD                       | 2140826        | 1   | 2140826     | 50.27   | 0       | 1   |
| CE                       | 5580570        | 1   | 5580570     | 131.04  | 0       | 1   |
| DE                       | 1337661        | 1   | 1337661     | 31.41   | 0       | 1   |
| ABC                      | 14719          | 1   | 14719       | 0.35    | 0.558   | 1   |
| ABD                      | 3068           | 1   | 3068        | 0.07    | 0.789   | 1   |
| ABE                      | 104233         | 1   | 104233      | 2.45    | 0.122   | 1   |
| ACD                      | 3931           | 1   | 3931        | 0.09    | 0.762   | 1   |
| ACE                      | 103246         | 1   | 103246      | 2.42    | 0.124   | 1   |
| ADE                      | 60917          | 1   | 60917       | 1.43    | 0.236   | 1   |
| BCD                      | 5545           | 1   | 5545        | 0.13    | 0.719   | 1   |
| BCE                      | 2050           | 1   | 2050        | 0.05    | 0.827   | 1   |
| BDE                      | 104438         | 1   | 104438      | 2.45    | 0.122   | 1   |
| CDE                      | 4366483        | 1   | 4366483     | 102.54  | 0.558   | 1   |
| Error                    | 2980971        | 64  |             |         |         |     |
| Total                    | 80936474       | 95  |             |         |         |     |
| R <sup>2</sup>           |                |     | 96.32%      |         |         |     |
| Adjusted R <sup>2</sup>  |                |     | 95.00%      |         |         |     |
| Predicted R <sup>2</sup> |                |     | 93.07%      |         |         |     |

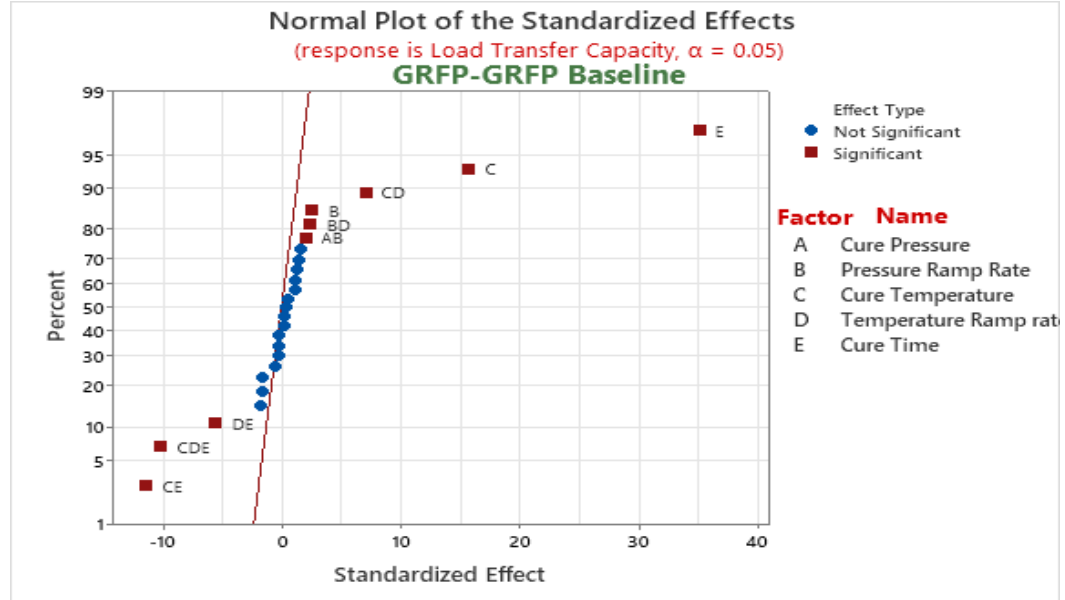


Figure 5.11 Normal Plot for Baseline Shear Strength of GFRP-SLJ's

An empirical model is presented in coded format to predict joint shear strength based on the statistical analysis of test data. Response equation based on coded factors allows the prediction of response by assigning +1/-1 levels to each independent process variable. In this study, the coded response is given by

$$\begin{aligned} \text{GFRP/GFRP Baseline LTC (N)} = & 5341.3 + 25.4 P + 53.7 R_p + 330.7 T + 32.2 R_t + \\ & 739.8 t + 42.4 P R_p - 5.4 P T + 10.1 P R_t + 27.6 P t + 27.6 P t - 3.5 R_p T + 51.7 R_p R_t - \\ & 36.5 R_p t + 149.3 T R_t - 241.1 T t - 118.0 R_t t - 12.4 P R_p T + 5.7 P R_p R_t + 33.0 P R_p t + \\ & 6.4 P T R_t - 32.8 P T t + 25.2 P R_t t + 7.6 R_p T R_t - 4.6 R_p T t - 33.0 R_p R_t t - 213.3 T R_t t \end{aligned} \quad (5)$$

Equation (5) gives the statistical prediction of the shear strength (N) of Baseline joints that have not been heat cycled. From Figure 5.12 (a) can be observed that residuals

follow a normal distribution, as a straight line is fitted through the normal plot of residuals. Figure 5.12 (b) is a plot of the residuals versus the experimental run order, checks lurking variables that may have influenced the response during the analysis. Random scatter must be obvious; blocking and randomization of testing would minimize the probability of trends that may invalidate the analysis.

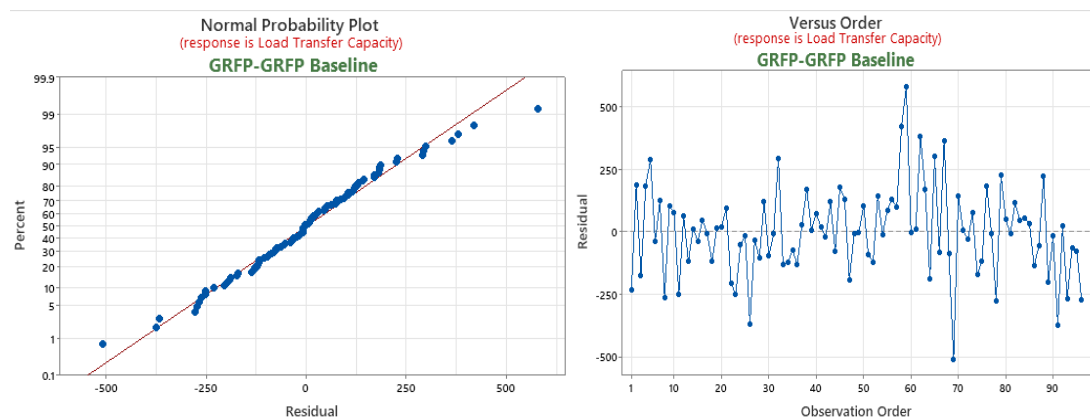


Figure 5.12 Baseline Static LTC of GFRP Joints  
(a) Normal Plot of residuals (b) Residual vs. Run

Figure 5.13 shows single-variable effect on Baseline shear strength. Lines with positive slopes indicates that increasing that factor would increase joint shear strength; the opposite is true as well. The value of the slope is a measure of how significant the factor is [14].

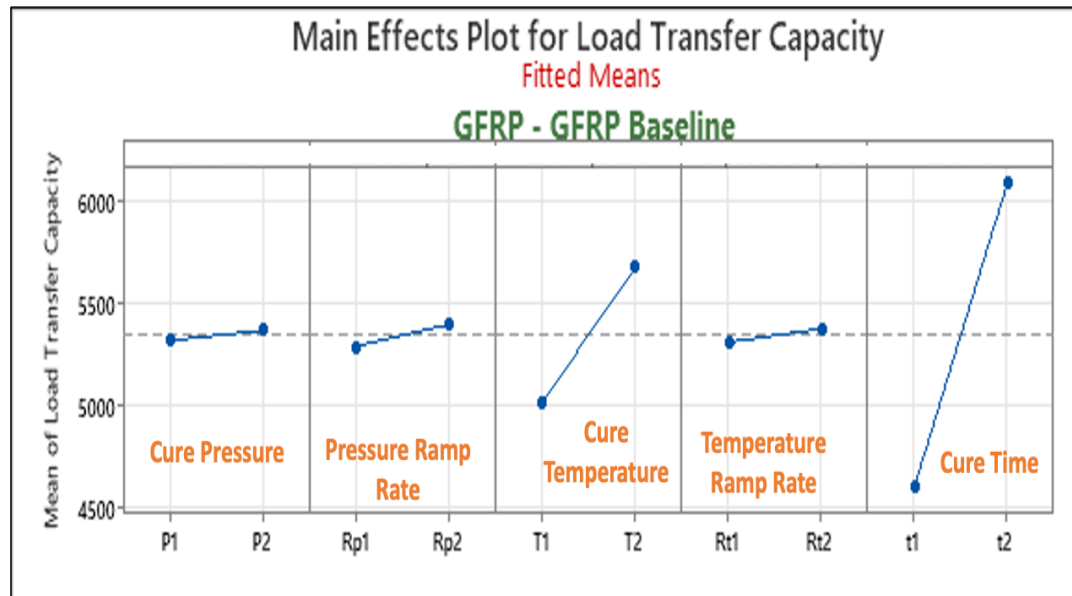


Figure 5.13 Single Variable Effect on baseline LTC of GFRP-SLJ's

## CHAPTER SIX

### CONCLUSION

The effect of cure process variables on Static performance and glass transition temperature of autoclave cured epoxy film adhesive is investigated. Autoclave process variables considered are cure temperature, cure pressure, cure time, temperature ramp rate, and pressure ramp rate. The experimental study offers the following observations and conclusions.

High cure temperature ( $T_2 = 260^\circ\text{F}$ ) have positive effect on LTC and  $T_g$  as compared low cure temperature ( $T_1 = 200^\circ\text{F}$ ) when combined with cure time ( $t_1$ ). But opposite effect was observed for high cure time ( $t_2$ ) process combined with high cure time. It's because with increase in cure temperature  $T_g$  continue to rise to almost linearly to reach vitrification. Beyond that increase in cure temperature or cure time results in thermal degradation of polymeric chains which have negative effect on the static performance of epoxy film adhesive joints.

It shows lower temperature ramp rate ( $R_{t1}$ ) have positive effect on the LTC as compared with high cure temperature ( $R_t$ ).  $R_{t1}$  ensures longer cure process and more mobility of monomers to increase cross linking and degree of cure ( $\alpha$ ).

High cure pressure ( $P_1$ ) results into higher static LTC,  $T_g$  when compared to low cure pressure ( $P_2$ ). High cure pressure results in formation of intermolecular hydrogen bonding between hydroxy groups and carbonyl groups also increased the interaction of the polymer chains which improve the cross-linking densities and the mechanical properties of the cured adhesive.

High cure time ( $t_2 = 100$  min) combined with low cure temperature ( $T_1 = 200$  °F) increased static performance of SLJ. Static LTC was lower for the cure process in combination  $t_2$ ,  $T_2$ ,  $R_{t1}$ . The thermal degradation or oxidative crosslinking (above the  $T_{g\infty}$  of the adhesive) is responsible for the decrease of strength with increasing curing time. When below the  $T_{cure}$  at which the  $T_{g\infty}$  is achieved, the static LTC and degree of cure ( $\alpha$ ) of the adhesive increases as the cure temperature increases. When above the  $T_{cure}$  at which the  $T_{g\infty}$  is achieved, there is an opposite behavior, i.e., the strength and stiffness decrease as the cure temperature increases.

$T_g$  and the mechanical properties have a similar behavior. It was found that the  $T_g$ , LTC, and degree of cure ( $\alpha$ ) vary as a function of the cure temperature of the epoxy adhesive. When cured below the  $T_{cure}$  at which the  $T_{g\infty}$  is achieved, the  $T_g$ , LTC, and degree of cure ( $\alpha$ ) increase as the cure temperature increases. When cured above the  $T_{cure}$  at which the  $T_{g\infty}$  is achieved, the  $T_g$ , LTC, and degree of cure ( $\alpha$ ) decrease as the cure temperature increases.

## CHAPTER SEVEN

### FUTURE WORK

From the research work presented in this dissertation, the future work is suggested as follows,

- Different process-controlled curing methods by autoclave to be explored using mpolycarbonate material or other materials with film adhesive to mechanically withstand harsh environmental conditions
- Investigate solar effect on adhesively bonded joints for its mechanical strength and failure mode as well as material property differences



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