

EFFECTS OF OUT-TIME ON CURE KINETICS AND RHEOLOGICAL PROPERTIES OF  
OUT-OF-AUTOCLAVE AND AUTOCLAVE PREPREGS

A Thesis by

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The following faculty members have examined the final copy of this thesis for form and content, and recommend that it be accepted in partial fulfillment of the requirement for the degree of Master of Science with a major in Mechanical Engineering.

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## DEDICATION

To my beloved parents, Mahmoud Habibi and Elaheh Mansouji, for their sacrifice and love throughout my life.

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## ABSTRACT

In aerospace applications, multiple rolls of prepreg are often used to manufacture large parts and the material is kept outside for several days during fabrication. This requirement raises issues for the fabrication of large parts where stacks of prepreg plies placed on a tool would remain at room temperature until the rest of the part is laid-up. As such, it is always a concern that the part's quality could be affected due to the material advancement in curing during out-time under ambient conditions. Although the reaction is more progressive at an elevated temperature, extended out-time at a lower temperature could also cause problems, such as a decrease in tackiness and the processability of prepreg.

This work presents results from a study that monitored changes in the viscoelastic properties and cure kinetics of two different carbon-epoxy prepreg resin systems that were advanced in aging under ambient conditions. An encapsulated-sample rheometer along with a differential scanning calorimeter was used to capture and characterize the out-time behavior of the prepreg for up to 40 days. The viscoelastic properties of prepreg such as storage modulus ( $G'$ ), loss modulus ( $G''$ ), complex viscosity ( $\eta^*$ ) and damping factor ( $\tan\delta$ ) were measured for samples with different out-times. Utilizing the rheology technique, a good correlation between the minimum viscosity time, gel-time, and out-time was obtained. Additionally, cure kinetic values including heat flow, degree of conversion ( $\alpha$ ), glass transition temperature ( $T_g$ ), sub-ambient glass transition temperature ( $Sub - T_g$ ) and activation energy were obtained to characterize the thermal properties of prepreg during out-time. It was observed that the sub-ambient glass transition temperature and the percent of conversion due to aging increased proportionally with respect to the out-time of the prepreg. Moreover, the total heat of reaction, peak temperature, and activation energy decreased as out-time increased.

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Composite Materials

Composite is a structural material combined of two or more constituents with significantly different chemical and physical characteristics. Although the final material will have characteristics different from the individual constituents, the individual components are immiscible and remain distinct within the finished structure. High strength/weight ratios and tailorability are the distinct characteristics of composite materials. The relative mechanical advantage of composites can be measured by two factors. The first parameter is referred to as the specific modulus, is defined as the ratio between the young's modulus (E) and the density ( $\rho$ ) of the composite. The second parameter is called the specific strength of composite and is defined as the ratio between the strength and density of the composite as follows[1, 2]:

$$\text{specific modulus} = \frac{E}{\rho} \quad (1)$$

$$\text{specific strength} = \frac{\sigma}{\rho} \quad (2)$$

Technically, composites consist of two phases, the continuous phase and the reinforcing phase. The reinforcing phase which is called reinforcement is the principal constituent. The reinforcement is typically in the form of fiber, which bears the major portion of the load due to its superior properties. The continuous phase is called the matrix. The matrix surrounds the reinforcement and sustains it inside the structure. Also the matrix bonds the fibers together and keeps them in their relative position.

Furthermore, there are important matrix factors that contribute to the mechanical properties of composites including protecting fibers against adverse environments and

distributing the load to fibers.

Usually, in aerospace application, the reinforcement is in the form of fibers. Fibers are the principle component of the composite structure and carry the major load and stress. Due to their high strength and stiffness, carbon fibers have been widely used in aerospace applications. Carbon fibers are filaments made from non-graphitic carbon which is produced by carbonization. [2-4]

## 1.2 Fiber-Polymer Composites of Epoxy Resins

Fiber-polymer composites are the most common composites used in aerospace industries, consisting of polymer resin as the matrix phase and the fibers as the reinforcement. Generally, polymers are classified as either thermosets or thermoplastics. Thermosetting resin systems should be cured using recommended time-temperature cure cycles to achieve their desired mechanical properties. For thermosetting resins, cross-linking and polymerization of the polymer molecules occur during the irreversible exothermic curing process.

Epoxy, a popular thermoset, is an organic resin with a low molecular weight. Epoxies are used as the most popular polymer matrix for many reasons:

- Low viscosity, which allows a completely wetting of fibers
- High Strength
- Availability
- Low volatility during cure
- Low shrink rates

Carbon fiber-epoxy composites are a popular type of fiber-polymer composites that are rapidly emerging in aerospace structures where the strength-to-weight ratio is critical.

### 1.3 Prepreg

Prepreg or pre-impregnated composite fibers is a broad, ready-made tape of woven or aligned fibers impregnated with a polymer resin. A laminated composite including complex geometries and curvatures can be fabricated by stacking layers of prepregs followed by curing.

Prepregs are available in width from 76 to 1270 mm and are manufactured by pulling a row of uniformly spaced fibers through the resin bath that contains epoxy resin dissolved in compatible solvent. Then the impregnated fibers are heated using an oven and advanced to the curing state which is called the B-stage. After reaching the B-stage the prepreg sheet is rolled in a release film. The fiber volume fraction is controlled by the type of the weave and number of tows brought into the resin bath. [5]

Currently, prepregs are predominantly used in aerospace industry, compared to the traditional wet methods, due to their high uniformity of fiber-resin distribution and reduced volatile vapor problems.

#### 1.3.1 Prepreg Storage, Handling and Out-time

To address the limitations associated with the processing of prepregs important definitions including storage life under specified conditions, handling life under ambient conditions, and out-time capability of laid-up material should be defined. The storage life or shelf life is the allowable time that the prepreg remains useful under its controlled storage environment and continues to meet specifications of its intended use. The out-time or out-life is the period of time that the prepreg remains useful outside of its recommended storage environment.

Per FAA regulations, it is recommended that a tracking of material be carried out by the material supplier to document out-time of material from the date the date of impregnation to the

arrival on the dock of the end-user. Figure 1 shows the recommended definitions based on FAA standards. The standard out-time was divided into handling life and staging life as shown in Figure 1

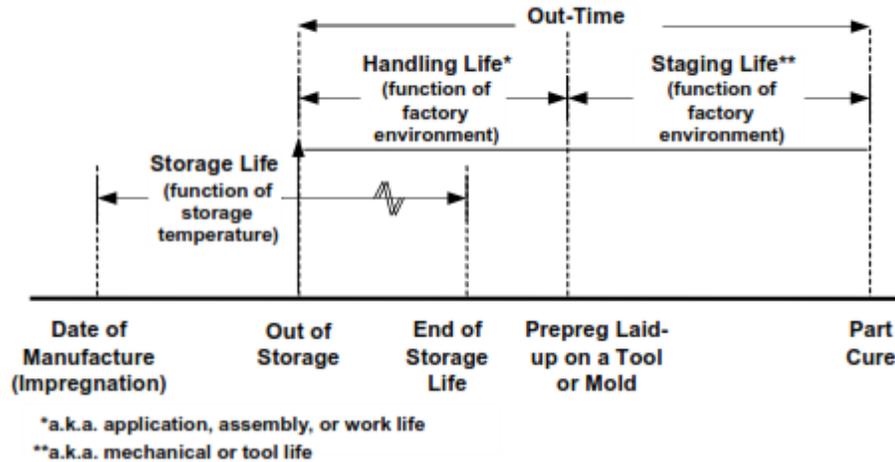


Figure 1. The Federal Aviation Administration definition for out-time (handling and staging life) and storage life.

### 1.3.2 Prepreg Processing

Generally, uncured epoxy resins do not have good mechanical, chemical and heat resistance properties. However, desired properties are achieved by reacting the linear epoxy resin with appropriate curatives to form three-dimensional cross-linked thermoset structures. This process is commonly called curing. Curing of epoxy resins includes an exothermic reaction and, if not controlled, might cause thermal degradation.

### 1.3.3 Autoclave Processing

In the current approach of curing composites autoclave processing is the most popular method used to manufacture aerospace structures. Autoclave is a pressurized vessel, where the

stack of uncured prepreg is cured using a relatively high pressure and temperature. During the autoclave processing the volatiles and porosities are sucked out of the laminate utilizing vacuum pressure. The autoclave product is a high-quality, void-free laminate.

#### 1.3.4 Out-of-autoclave Processing

Out-of-autoclave composite processing has been used for the manufacture of aerospace structures and prototypes since the 1990's. To reduce the delivered part cost and to overcome the production limitations associated with tooling, the first generation of out-of-autoclave prepregs was designed for low cure temperatures. The potential to manufacture large structures has removed the size constraints and has led to extensive use of out-of-autoclave prepregs. Recently, the out-of-autoclave process has progressed to a state of the art autoclave curing process, although the maximum applying pressure does not exceed 1 atmosphere. In contrast, autoclave processing requires high temperature and high pressure equipment, which increases the final cost. During vacuum bag curing, the resin uses elevated temperatures to flow into the dry regions while the entrapped air is removed from the uncured prepregs.[6-8]

##### 1.3.4.1 Cure and Debulking Process

Out-of-autoclave prepreg was designed to be vacuum bag cured with two-step cure cycles. The first step could be a wide range of low temperatures 80-130 °C to proceed to a free-standing post cure temperature at 180 °C. The first step is referred to as intermediate cure temperature was intended to consolidate the laminate .The second step is a free-standing post cure temperature to reach the fully cross-linked structure.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Thermal Analysis of Polymers

Thermal analysis is a family of measurement techniques utilized to study the cure kinetics and characterize the thermal properties of materials. In the case of polymers, thermal analysis measures the physical properties of material to build a connection between temperature and physical properties of material. TA has been used as the main method for characterization and design purposes in polymeric composites.[9]

Differential scanning calorimetry (DSC), which is defined as a quantitative differential thermal analysis technique, is the most popular technique of thermal analysis. Although this method has existed since 1963, recently this technology has progressed significantly. ASTM Standard E473 defines the DSC as a technique in which the heat flow difference into a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled-temperature program. With the advancement of mechanical heating and cooling systems, relatively low and high temperature measurement is feasible by DSC. [10, 11]

##### 2.1.1 Degree of Cure

Degree of cure is a measure of the extent of cross-linking and 3D network formed in the structure of composite. The state of a thermosetting prepreg resin during cure due to polymerization is referred to as the degree of cure  $\alpha$ . Technically the degree of cure ( $\alpha$ ) measures the progress of reaction with respect to the fully cured state. In the literature, a number of studies have developed models for the degree of cure,  $\alpha$ . The modeling of conversion is of

great importance since it reveals a number of facts that aid in the interpretation and understanding of the behavior of material.[12-14]

For thermosetting resin systems the cure process is an exothermic reaction in which the reactants turn into the products and release some heat. The heat of reaction represents the progress of the reaction and the state of the material during cure and can be calculated as:

$$H(t) = \int_0^t \left( \frac{dQ}{dt} \right) dt \quad (3)$$

Where,  $H(t)$  is the amount of heat released up to time  $t$  and  $\left( \frac{dQ}{dt} \right)$  is the rate of heat generation.

In thermal analysis, dynamic and isothermal scanning are the most common techniques used to obtain the heat of reaction. Figure 2 shows the area under the heat flow curve integrated by a linear baseline using dynamic and isothermal scanning.

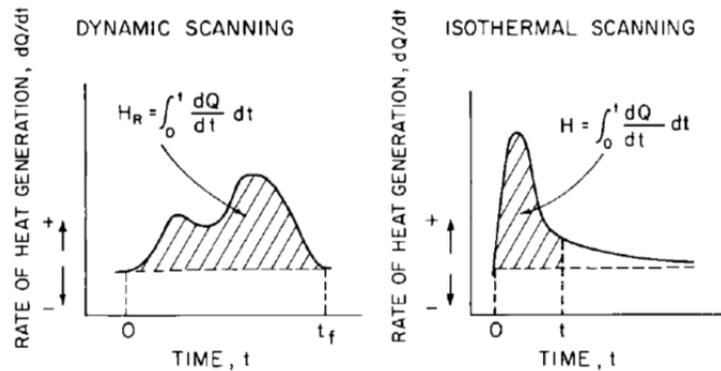


Figure 2. Dynamic and isothermal scanning techniques used to calculate the heat of reaction.[15]

Also  $H_U$ , the ultimate heat of reaction, is defined as:

$$H_U = \int_0^{t_f} \left( \frac{dQ}{dt} \right) dt \quad (4)$$

Where  $t_f$  is the time required to complete the reaction.

From previous studies, different methods were found for the calculation of degree of

cure. Due to the inconsistency of ultimate heat of reaction and also the methodology of calculation, various equations were developed to model degree of conversion. Although some researchers stated that the ultimate heat of reaction is independent of the cure profile[16], others believed it depends on cure cycle[17]. Among these techniques the following equations were found to be more common in literature [15, 18-22]:

$$\alpha(t) = \frac{1}{H_U} \int_0^t \left( \frac{dQ}{dt} \right) dt \quad (5)$$

$$\alpha(t) = \frac{H(t)}{H_U} \quad (6)$$

Where,  $H_U$  is the ultimate heat of reaction obtained from dynamic scan and,  $dQ/dt$  is the rate of heat generation obtained from DSC dynamic scanning. The use of the above equations could be limited to dynamic scanning due to the inconsistency of the values obtained for ultimate heat of reaction,  $H_U$ .

$$H_U = H_t + H_R \quad (8)$$

To address the shortcomings of the aforementioned approach, some scholars modified the above equations based on the definition of the residual heat of reaction,  $H_R$ . In this approach the degree of cure can be calculated using following equation [23, 24]:

$$\alpha = \frac{H_U - H_R}{H_U} = 1 - \frac{H_R}{H_U} \quad (8)$$

Here,  $H_R$  is the residual heat of reaction obtained from an isothermal scanning on partially cured sample and  $H_U$  is the ultimate heat of reaction obtained from DSC dynamic scanning. This model can only estimate the final degree of cure while utilizing  $H(t)$  approach, both the final

degree of cure and the real time degree of cure (the degree of cure during cure) can be calculated. The scholars stated that the  $H_R$  method gives an accurate estimation of  $\alpha$  while the  $H(t)$  approach needs infinite experiment time and more runs to generate consistent data. For each isothermal temperature there should be an identical number of experiments to measure the corresponding  $H_R$  accurately in order to build the model. Both techniques could be used simultaneously for validation and comparison purpose.

Hubert et al. and Kim et al. modified the equations above and presented a new model for  $\alpha$  that was more focused on isothermal curing, which is also called the “isothermal degree of cure”  $\beta$ . [13, 25]

$$\beta(t) = \frac{1}{H_t} \int_0^t \left( \frac{dH(t)}{dt} \right) dt \quad (9)$$

Here  $H_t$  is the ultimate heat of reaction obtained from an isothermal cure cycle with infinite time. In this equation the residual heat of reaction was not taken into consideration. The isothermal degree of cure  $\beta$  is a new approach in modeling the cure kinetics of composites and it could be used along with previous established techniques. The following equation connects the term  $\alpha$  to  $\beta$ .

$$\alpha(t) = \beta(t) \frac{H_t}{H_U} \quad (10)$$

As mentioned before preregs are advanced in curing to the B-stage for ease of processing and handling. Thus the initial degree of cure is not zero but is assumed to be zero in practice. The modified degree of cure,  $\alpha_m$  for a B-stage prepreg can be obtained using the following equation [10, 18]:

$$\alpha_m(t) = \alpha_0 + (1 - \alpha_0)\alpha(t) \quad (11)$$

Where  $\alpha_m$  is the modified degree of cure,  $\alpha_0$  is the initial degree of cure and  $\alpha(t)$  is the degree of cure obtained using equation 5.

### 2.1.2 Kinetic Models

To address the kinetic characterization of polymeric composites, several mathematical equations have been developed in the literature. A variety of kinetic models have correlated the chemical reactions to time and temperature and degree of cure. In some literature the cure kinetic characterization of polymers was classified as mechanistic and phenomenological (empirical) models. Phenomenological models are mathematical expressions which ignore how the reacting groups are converted to products. In contrast, mechanistic models take into consideration the several reactions occur during the cure process. Although mechanistic models are expected to predict the cure kinetics accurately, sometimes it is not feasible to build these models due to the complexity of cure reactions. Thus phenomenological models are more popular in the study of cure kinetics [16, 26, 27].

#### 2.1.2.1 Phenomenological(Empirical) Models

A phenomenological model is obtained from a relatively simple rate equation. Some models simply describe the cure process as one reaction. The general phenomenological model is expressed by[27-30]:

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \quad (12)$$

In this equation,  $K(T)$  is the reaction rate constant which depends on the cure time and  $f(\alpha)$  is the function of the degree of cure. Usually, the rate constant is expected to be in the form of

Arrhenius which is a function of cure temperature:

$$K(T) = Ae^{-E_a/RT} \quad (13)$$

Here  $A$ , is the pre-exponential constant which is independent of the cure temperature,  $R$  is the universal gas constant,  $E_a$  is the activation energy, and  $T$  is the absolute temperature.

The term  $f(\alpha)$  is known as conversion function, and it indicates the type of reaction and heat flow rate. The cure mechanism for epoxy resins change from being kinetically controlled in the beginning of the cure reaction to diffusion controlled in the end of the reaction. Several models were proposed in the literature such as  $n^{\text{th}}$  order model and autocatalytic model.

The  $n^{\text{th}}$  order model predicts the maximum rate of reaction to occur at the start of reaction ( $\alpha = 0$ ). The efficiency of the autocatalytic models has been evaluated by many workers. According to literature this model is not capable of predicting the progress of the entire reaction. The  $n^{\text{th}}$  order model is generally given by [10, 27, 28, 30]:

$$f(\alpha) = (1 - \alpha)^n \quad (14)$$

In this equation  $n$  is the reaction order.

The Kamal model which takes into account the autocatalytic reaction has been widely used in the literature [30-32]:

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1 - \alpha)^n \quad (15)$$

In this equation,  $m$  and  $n$  are the reaction orders and are independent of temperature.

## 2.2 Viscoelasticity

A material is said to be viscoelastic when it exhibits both elastic and viscous behavior when undergoing deformation. Basically, the combination of the theory of elasticity and viscosity governs the behavior of a viscoelastic material. According to Hooke's law, for perfectly

elastic solids undergoing small deformations, the stress is always proportional to the strain. These materials are generally categorized as Hookean or linear-elastic. Additionally, for viscous liquids based on Newton's law, the stress is always proportional to rate of strain and is independent of the strain itself. When a viscoelastic material undergoes sinusoidal loading the response is not in-phase with applied stress and show significant deviations from Newton's and hook's law. Furthermore, the viscoelastic material stores a part of the energy and dissipates the rest in each cycle. If the stress-strain relation can be explained by linear differential equations the material is said to be linear viscoelastic. Hence the ratio of stress to strain is a function of frequency alone and is independent of stress magnitude. [33]

The foundation of linear viscoelasticity is based on the phenomenological theory of creep and stress relaxation. In general, the stress relaxation is the property of viscoelastic polymers. Stress relaxation is defined as the decrease in stress when the material is subjected to constant strain. Figure 3 shows the stress relaxation under constant strain. [34]

On the other hand, the creep is the increased tendency towards strain which, if held at constant stress, results in plastic deformation.[35]

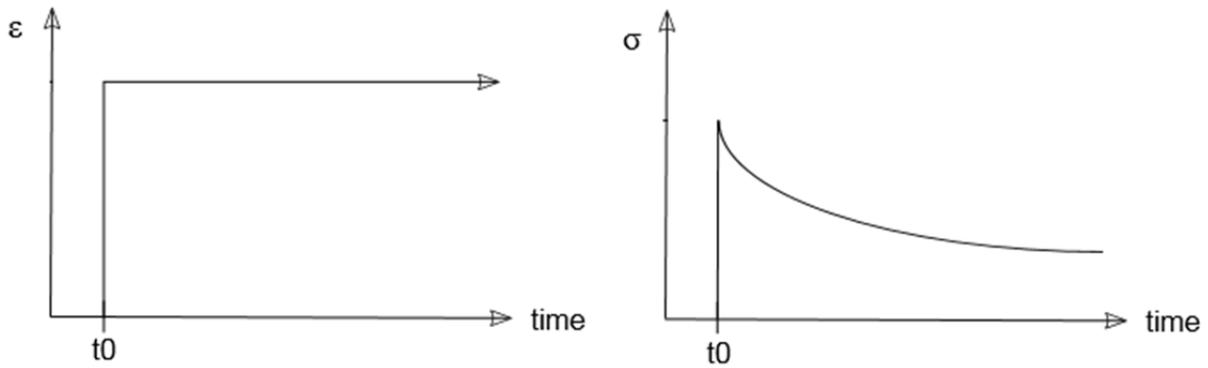


Figure 3. Stress relaxation phenomena in viscoelastic materials occur when the stress decreases while the strain is held constant.

Basically, for elastic materials, the ratio of the shear stress to corresponding strain is referred to as shear modulus  $G$  and is defined as  $\sigma/\gamma$ . The relaxation modulus  $G(t)$  is time dependent and can be obtained as:

$$G(t) = \sigma(t)/\gamma \quad (16)$$

Here  $\gamma$ , is the shear strain and  $\sigma(t)$  is stress. In contrast in creep phenomena the dependence of strain  $\gamma$  on time can be obtained from:

$$\gamma(t) = \sigma J(t) \quad (17)$$

Where,  $J(t)$  is defined as the creep compliance and has the dimension of reciprocal modulus. For a perfectly elastic material  $J = 1/G$ . [33]

### 2.2.1 Mechanical Modeling of the viscoelastic behavior

The time dependent relaxation modulus  $G(t)$  and creep compliance  $J(t)$  can be expressed as a mechanical element (spring) and a viscous elements (dashpot). Maxwell modeled the viscoelastic system with spring and dashpot in series. In contrast, Kelvin's model includes a spring and dashpot arranged in parallel.

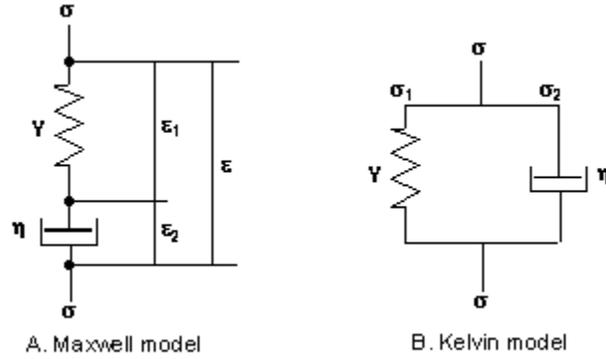


Figure 4. Maxwell's and Kelvin's viscoelastic models[33].

### 2.2.2 Viscoelastic Parameters

For a viscoelastic material subjected to a sinusoidal stress at a frequency of  $\vartheta$ , the applied shear strain can be expressed as[36]:

$$\gamma = \gamma_0 \sin(\omega t) \quad (17)$$

Where  $\gamma_0$  is the maximum amplitude of strain and  $\omega=2f$  is the angular frequency of the strain.

For a linear viscoelastic system the strain will also alternate sinusoidally but will be out of phase with the stress. Thus the stress response  $\tau$  of the viscoelastic material, will be sinusoidal and is expressed as[33, 37, 38] :

$$\tau = \tau_0 \sin(\omega t + \delta) \quad (18)$$

Here  $\tau_0$  is the maximum amplitude of the stress, and  $\delta$  is the phase lag between stress and strain.

For a perfectly elastic material  $\delta=90^\circ$ , while for a pure viscous material  $\delta=0^\circ$ , and for a viscoelastic material  $0^\circ < \delta < 90^\circ$ . By expanding the equation (18):

$$\tau = (\tau_0 \cos \delta) \sin(\omega t) + (\tau_0 \sin \delta) \cos(\omega t) \quad (19)$$

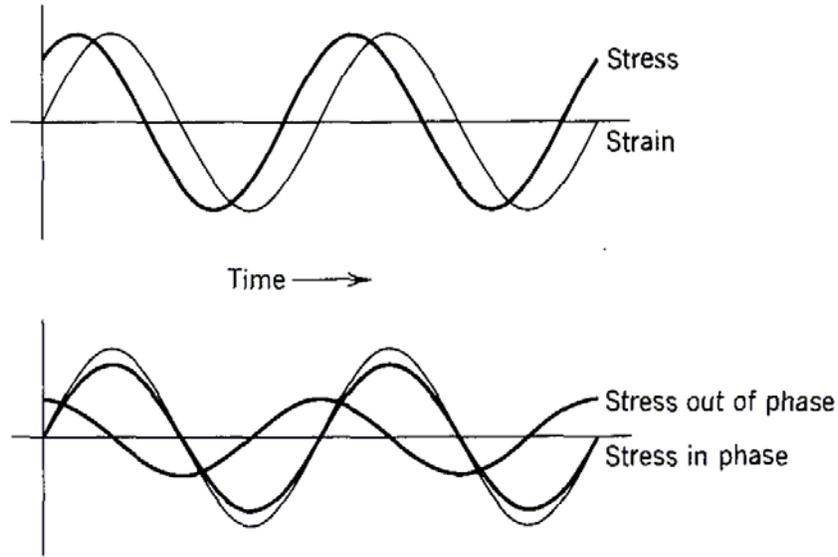


Figure 5. The in-phase and out-of-phase response of the stress to applied sinusoidal strain[33].

By dividing the two sides of equation 19, by maximum strain, the shear modulus will be:

$$G = G'(\omega) \sin(\omega t) + G''(\omega) \cos(\omega t) \quad (20)$$

Where  $G$  is the shear relaxation modulus,  $G' (= \tau_0 \cos \delta / \gamma_0)$  is the storage modulus, which represents the elastic property of the viscoelastic material, and  $G'' (= \tau_0 \sin \delta / \gamma_0)$  is the shear loss modulus, which represents the viscous property of viscoelastic material.  $\tan \delta$  is the tangent of the phase lag,  $\delta$  and is equal to the ratio of the storage modulus to loss modulus,  $G''/G'$ . Theoretically,  $\tan \delta$  expresses the energy dissipation. In some literatures complex modulus of a viscoelastic material was expressed as:[33]

$$\tau^* / \gamma^* = G^* = G' + iG'' \quad (21)$$

Thus

$$|G^*| = \tau_0 / \gamma_0 = \sqrt{G'^2 + G''^2} \quad (22)$$

The term  $G^*$  is the complex modulus consisting storage and loss modulus.

## 2.3 Viscoelastic Transition of Thermosetting Resin

### 2.3.1 Gelation

Gelation, the irreversible transformation of a viscous liquid to an elastic gel, is the most significant characteristic of thermosets. Gelation is critical in the processing of polymeric composites since the resin is no longer able to be processed beyond this point. Theoretically, gelation is identified as the rapid approach to an infinite viscosity or the dramatic increase of molecular weight of polymer chains in the thermosetting mass. After the gel point, the formation of cross-linked network begins and proceeds toward infinity. From the processing point of view, this phenomenon is the most important transition in the curing process of thermosetting resins. Usually gelation happens at between 55% and 80% of conversion and depends on the functionality and reactivity of the reactants.[39]

Gelation occurs at a well-defined stage of chemical reaction and thus does not stop the cure process (the reaction rate does not change). Therefore, utilizing the techniques that are only sensitive to chemical reactions will not aid in detecting the time of reactions. In rheology, the gel point is identified by the peak of  $\tan\delta$  where the complex viscosity tends to infinity. Some other scholars believe that the interception point of shear storage modulus ( $G'$ ) and shear loss modulus ( $G''$ ) is the gel point ( $\tan\delta = G''/G' = 1$ ). Flory (1953) stated that the gel point occurs at a critical degree of conversion,  $\alpha_{gel}$  for an epoxy resin and is independent of temperature. [39-42]

### 2.3.2 Vitrification

Vitrification is a distinct phenomenon in the curing process of thermosetting resin and is a phase transition in which the resin changes from a glassy stage to an elastic gel or viscous liquid and vice versa. Vitrification can be identified as a decrease in the reaction rate when it changes from the kinetically controlled to the diffusion controlled. Unlike the gelation, vitrification is a reversible transition that can occur at any stage of cure. Theoretically, vitrification is defined as the point where the glass transition of the growing chains or cross-linked network becomes coincidental to the cure temperature ( $T_g = T_{cure}$ ). Vitrification is detected by an increase in heat capacity obtained by modulated DSC (MDSC) or dramatic change in storage modulus by DMA.[39, 43]

### 2.3.3 Time-Temperature-Transformation (TTT) Diagram

The Time-temperature-transformation diagram was first presented by Gillham (1980) and Enns et al. (1981). This plot demonstrates the phase transformations in the curing process of thermosets as a function of isothermal temperature. A TTT cure diagram illustrates the state of the material, as a function of isothermal cure temperatures at different stages of the cure process. Figure 6 is a TTT diagram showing 4 phase transitions during the cure process of an epoxy resin. The dashed line represents the gelation line which shows when material changes from liquid to rubber state. On the other hand, the solid line is where the material changes from a rubber state to a glassy solid. As shown in figure 6, for temperatures below the glass transition temperature, where resin is unreacted, the reaction is limited to a solid state and thus is very slow. For  $T_{c_0} < T_{cure} < T_{c_{gel}}$  the resin will react until the glass transition temperature, which is continuously increasing, becomes equal to the cure temperature. At this point, the vitrification

occurs and the reaction rate will become diffusion controlled. For  $T_{c_{gel}} < T_{cure} < T_{c_{\infty}}$  the gelation precedes vitrification and a cross linked network begins to form until the glass transition temperature becomes equal to the cure temperature. [44, 45]

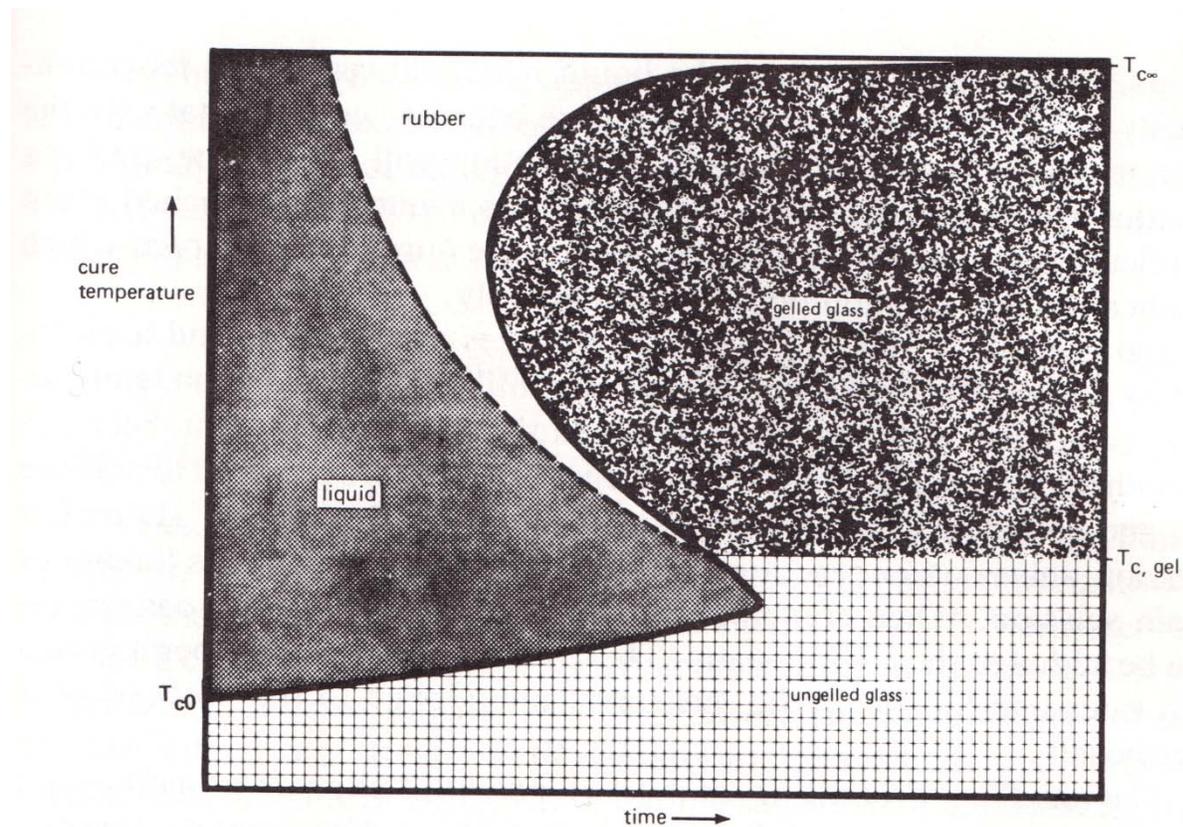


Figure 6. Time-Temperature-Transformation (TTT) diagram[39]

#### 2.4 Glass Transition Temperature

Glass transition is a distinguished transition in the cure process of polymers and it involves a reversible transformation from a glassy to a rubbery state and vice versa. The temperature at which the polymer undergoes this transformation is defined as the glass transition temperature. Above the  $T_g$ , the polymer chains have relative mobility and thus the material has a rubbery state. The determination of glass transition temperature is of paramount importance for

the design, manufacturing and service purposes. As the chemical reactions progress during cure, the glass transition temperature increases from a value of uncured reactants,  $T_{g_0}$  to a value of fully cross-linked network,  $T_{g_\infty}$ .  $T_{g_0}$  is defined as the temperature at which no significant reaction of uncured resin occurs due to the immobilization of reactive species. At the early stages of the cure process, the chemical reactions are kinetically controlled and, thus, occur at high rate. Though the polymer chains begin to form and cross-link with each other. Therefore, the  $T_g$  values increase at a relatively fast rate as the cure progresses. However, after the vitrification the chemical reactions become diffusion controlled. At this point,  $T_g$  increases gradually and reaches a plateau value.

## 2.5 Viscoelastic Modeling of Prepreg

The viscoelastic modeling of polymers during cure has been of paramount importance in composite manufacturing since the viscoelastic behavior of polymer resin dominates the final mechanical properties. Fundamental to this goal is the complete understanding of the transitions that occur during the cure of a polymer composite such as resin infusion, gelation and vitrification. Valuable models were found in the literature that focused on complex viscosity. Viscosity of a thermosetting resin plays a major role in the process modeling of polymer composite. Basically, the viscosity of a polymer depends on the state of cure which is a function of temperature. Thus advanced models include model variables such as temperature and degree of cure.

Dusi et al. modeled the viscosity of thermosetting resin as[46]:

$$\eta^* = \eta_a \exp(k' \alpha) \exp\left(\frac{U}{RT}\right) \quad (23)$$

Here  $\eta^*$  is the complex viscosity,  $\alpha$  is the degree of cure,  $U$  is the activation energy,  $\eta_a$  and  $k'$  are

constants which are assumed to be independent of temperature,  $R$  is the universal gas constant, and  $T$  is the absolute temperature. Constants are found by curve fitting.

Kenny et al. incorporated the degree of cure in his viscosity model as:

$$\eta^* = A_\mu \exp\left(\frac{E_\mu}{RT}\right) \left[ \frac{\alpha_g}{\alpha_g - \alpha} \right]^{A+B\alpha} \quad (24)$$

Where  $\alpha$  is the degree of cure,  $\alpha_g$  is the degree of cure at gelation,  $\eta^*$  is the complex viscosity,  $R$  is the universal gas constant,  $T$  is the absolute temperature,  $E_\mu$  is the activation energy, and  $A_\mu$ ,  $A$ ,  $B$ , and  $E_\mu$  are constants of the model which are, obtained by curve fitting.

It was found in the literature that glass transition temperature and isothermal cure time were also incorporated in viscoelastic models.[16, 47]

## 2.6 Problems Description in the Processing of Prepregs

In aerospace applications, multiple rolls of prepreg are often used to manufacture large parts and the material may remain outside for several days during fabrication. As such, it is always a concern that, under ambient temperature, the part's quality could be affected. Although the reaction is more progressive at elevated temperatures, extended out-time at lower temperatures could also build up problems, such as decrease in tackiness and the ability to process the prepreg. Also premature cure advancement of the prepreg within out-time could alter the cure kinetics and viscoelastic properties of the material, and result in inhomogeneous cure throughout the laminate.

Theoretically, the cure kinetic of epoxy resin does not begin until the material is elevated to certain temperature. However, since prepreg's epoxy is in B-stage, the reaction may also take place at lower temperature, although it happens slowly [48, 49]. As such, the allowable out-time is often of concern. Out-time depends on certain environmental conditions, such as temperature

and moisture. For that reason, the prepreg's expiration time might not be the same as the manufacturer specifications. To avoid using the expired material, many high-end users are monitoring and tracking both prepreg's out-time as well as the environment's conditions. Nevertheless, monitoring time and environmental conditions may not reflect the real kinetic reactions associated with out-time, and in many cases, the user may end up using the expired material or disposing of unexpired material. Therefore, understanding kinetic reaction at ambient temperature is vital to monitor the out-time effect of prepreg.

## 2.7 Out-time Study

Prepregs are the most popular form of composite materials supplied for aerospace applications [50]. The wide use of prepregs in the aerospace industry makes it imperative to push the out-life of the material, especially for large parts since they require more time for layup. These prepregs have to be stored below certain temperature before the layup, usually 0 °F (-19 °C), to limit the amount of premature curing. As mentioned premature cure advancement of the prepreg is of great importance both for manufacturers and end consumers. In addition, it is very difficult to track the out-life during handling from the production floor to storage, during shipment from manufacturer to the consumer site, during lay-up, and during thawing between the consecutive uses of the material from the same roll of the material.

There are several methods that have been studied for monitoring the aging of prepreg, including differential scanning calorimetry, mid-infrared spectroscopy, rheology, dynamic mechanical analyses, and photoacoustic spectroscopy [49, 51]. Premature advancement to the aging of polymeric prepregs has raised several issues in the processing of the prepreg [48, 52-56]. Previous studies have shown differential scanning calorimetry and rheometry are effective methods for characterizing the cure kinetics of prepreg.

Viscoelastic properties during cure play a vital role in the final mechanical properties of the composite laminates. Uncontrolled cure may cause undesired and excessive thermal and rheological variations that can induce microscopic and macroscopic defects in the composite part [53]. The cure recipe for different composite material can be different and can also vary for different applications. For example, the polymeric composite curing for high tech applications are performed at elevated temperatures to achieve enviable mechanical properties. However, in repair applications, it is desirable to cure the patch at a lower temperature to minimize heat damage to the surrounding material.

The effect of ambient storage on prepregs has been studied by many researchers. Chandrakala et al. [57] studied the effect of ambient storage on thermal and mechanical properties on composite laminate. They found a decrease in resin flow and mechanical properties with no change in glass transition ( $T_g$ ) for the aged material. de la Fuente[58] analyzed the accelerated thermal aging behavior in high performance energetic composite materials. Gu et al. [59] studied the effect of resin storage on rheological properties and the consolidation of composite laminates. Yu et al. [51] studied different epoxy prepregs aged under various conditions by near-infrared (NIR) and mid-infrared (MIR) Fourier transform spectroscopies, dynamic mechanical analysis (DMA), rheological analysis, time-resolved light scattering (TRLS), and optical microscopy (OM). Based on the previous studies, the main effect of aging on uncured thermosetting matrix prepregs was a gradual increase of viscosity during storage time as a consequence of the slow advancement of the curing reaction. This leads to losses in reactivity and process window that can irreversibly impair the performance of the composite [53].

## 2.8 Scope of this Work

The study, although not explored in literature is an evaluation of prepreg processability and cure kinetics development during out-time. What is needed is the assessment of the changes in material properties such as complex viscosity, storage modulus utilizing the rheology and thermal analysis. Additionally the comparison of different resin systems and validation of data seams necessary in the study of cure kinetics and viscoelastic properties of thermosetting preregs. Fundamental to these goals is an understanding of the transitions, occur during out-time, throughout measuring and analysis. The next chapters outline the scope of this work.

## CHAPTER 3

### EXPERIMENTATION AND METHODOLOGY

#### 3.1 Proposed Approach

To overcome the shortcomings associated with processability and mechanical properties of composites, an out-time study on cure kinetics and rheological properties of carbon-epoxy prepreg was proposed to overcome the shortcomings associated with the processability and mechanical properties of composites. Rheological and thermal analyses are two main techniques used in this study to characterize the out-time behavior of prepreg.

#### 3.2 Material

A commercial carbon fiber-epoxy prepreg, Cycom 5320 8HS manufactured by Cytec, was used to study the out time. This out-of-autoclave prepreg is a toughened epoxy resin system, reinforced by 8-harness satin (8HS) carbon fiber and designed for low curing temperature. It can be vacuum-bag cured to produce autoclave quality parts with a very low porosity level.

IM7-8552 prepreg resin system was used as an autoclave resin system. Hexcel IM7-8552 is an amine cured, toughened epoxy resin system supplied with woven carbon fibers. It is a high performance tough epoxy matrix with an out-life of 21 days at room temperature. It exhibits good impact resistance and damage tolerance for a wide range of applications [3].

#### 3.3 Conditioning

To conduct out-time study, the material was kept out of a freezer inside a plastic bag along with the desiccant to minimize the moisture effects, while the ambient storage temperature was  $23 \pm 5$  °C. In order to maintain consistency among the samples and to circumvent the moisture exposure, samples were stored under ambient conditions in a sealed nylon bag along

with the desiccant. The ambient temperature during the storage period remained in the range of  $21 \pm 3 \text{ }^\circ\text{C}$  with  $55 \pm 10 \%$  relative humidity. Figures 7-8 show the storage schematic and the arrangement used for this study.

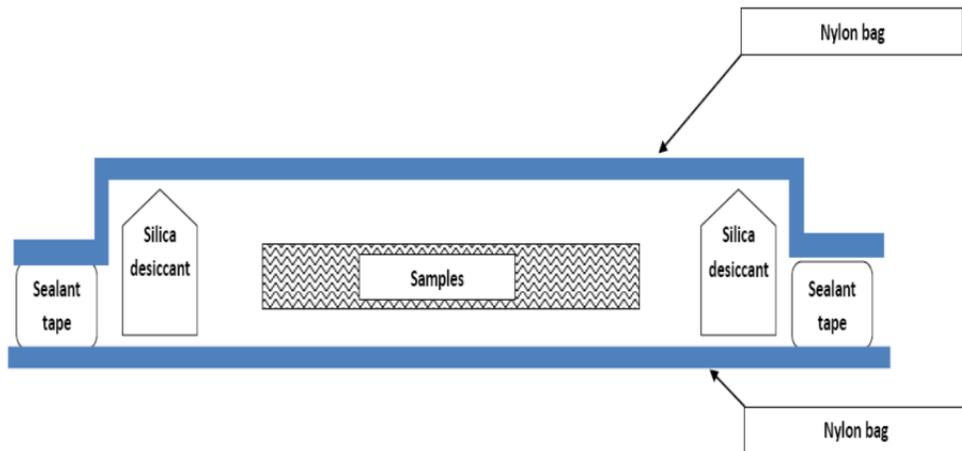


Figure 7. The Storage schematic for samples under ambient conditions.

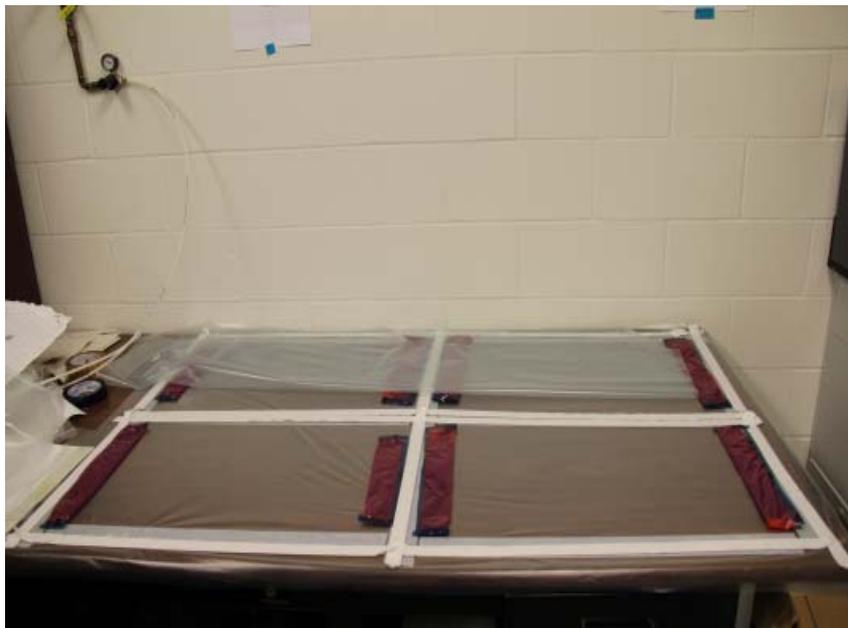


Figure 8. The storage arrangement for samples under ambient conditions.

### 3.4 Thermal Analysis

Thermal analysis is a group of experimental and analytical techniques that characterize the thermal properties of materials. In the study of polymeric composites, these techniques connect the cure temperature to the physical properties of prepreg. Differential Scanning Calorimetry (DSC) is the main technique used in this work to track the out-time behavior of prepreg.

#### 3.4.1 Differential Scanning Calorimeter (DSC)

Differential scanning calorimeter, or DSC, is one of the major instruments used in the thermal characterization of polymeric composites. It has been used widely to study the cure kinetics of prepreps. DSC also provides useful data which connects the reaction and transitions during the cure to time and temperature. Technically, temperature is the only measured parameter in DSC. It measures the difference in the heat flow rate between a sample and an inert reference material as a function of time and temperature.

In this work thermal analysis was carried out using TA Instruments Q2000 DSC. The Q2000 is an advanced DSC with an excellent performance in baseline flatness, precision, sensitivity, and resolution. Q2000 has 50 sample positions and auto-sampler that has made this instrument more popular in the study of cure kinetics for polymeric composites. Figure 9 schematically shows the Tzero cell design.

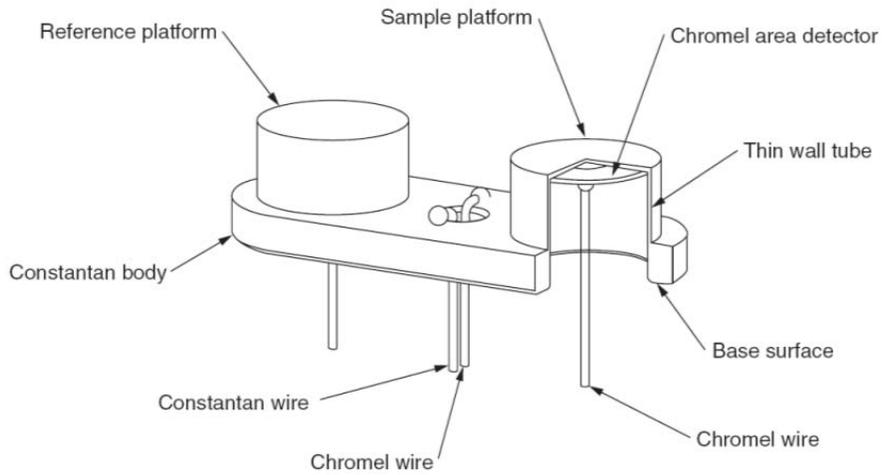


Figure 9. Schematic of the Tzero cell design.

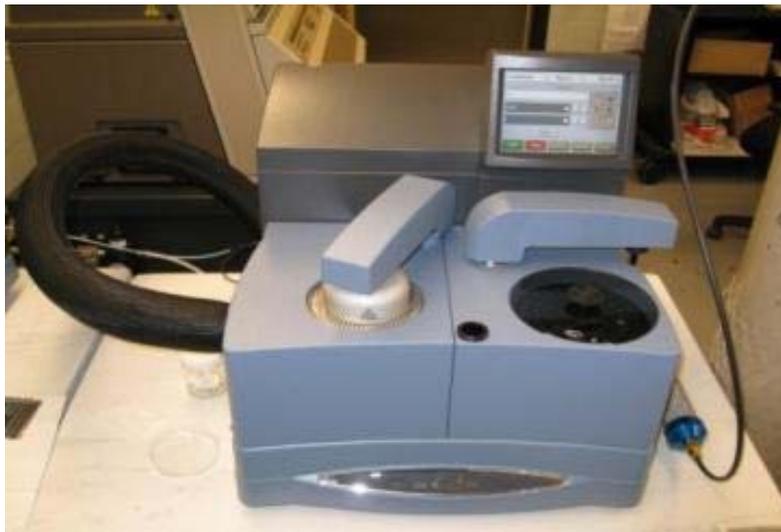


Figure 10. The TA Q2000 Differential Scanning Calorimeter.

### 3.4.1.1 DSC Samples

The uncured prepreg samples weighed between 10 and 15 mg and were punched first and was kept under a conditioning bag on order to reach the desired out-time. Then, the encapsulated samples in Tzero™ aluminum pans were subsequently cured in the DSC. All the samples with different out-time days, up to 40 days, were tested using a two-step cure cycle and a dynamic scan.

### 3.4.1.2 DSC Cure Cycles

DSC is capable of applying high heating rates up to 100°C/min to achieve desired temperatures. Dry nitrogen with a constant rate of 50 mL/min was used as purge gas. DSC cure cycles were designed based on both manufacturer and aircraft industries recommendations to achieve desired mechanical properties.

### 3.4.1.3 5320-8HS Out-of-autoclave prepreg

To study the effect of out-time on the properties of 5320 8HS out-of-autoclave prepreg resin, a two-step cure cycle was utilized which was recommended by the prepreg manufacturer (Figure 12). A dynamic scan was also used to obtain the total heat of reaction. The two-step cure cycle consists of two heat up rates (ramp rate) followed by isothermal stages. The first step was designed to be a low temperature cure for consolidation purpose followed by post cure temperature to obtain the perfect cross-linking. During the isothermal stage the temperature was constant while the ramp rate temperature was increasing in a constant slope. The cure cycle including first ramp rate, intermediate-cure, second ramp rate, and post-cure, and cool down rate were the same for different out-times. Figure11 shows a typical dynamic scan used to carry out thermal experiments on 5320-8HS. This plot consists of two dynamic scans that were used to obtain the total heat of reaction, the degree of cure and the glass transition temperature.

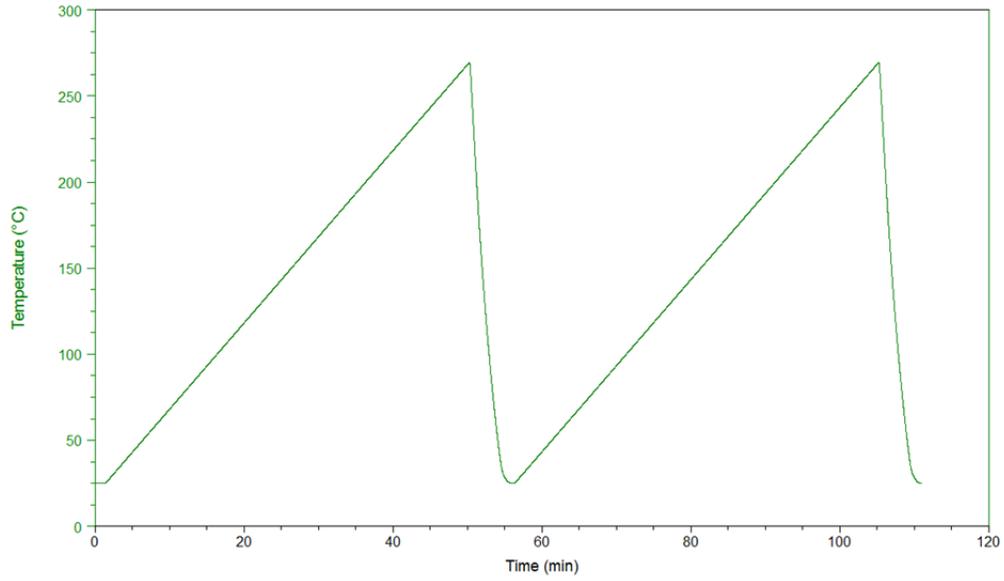


Figure 11. Typical DSC dynamic scan.

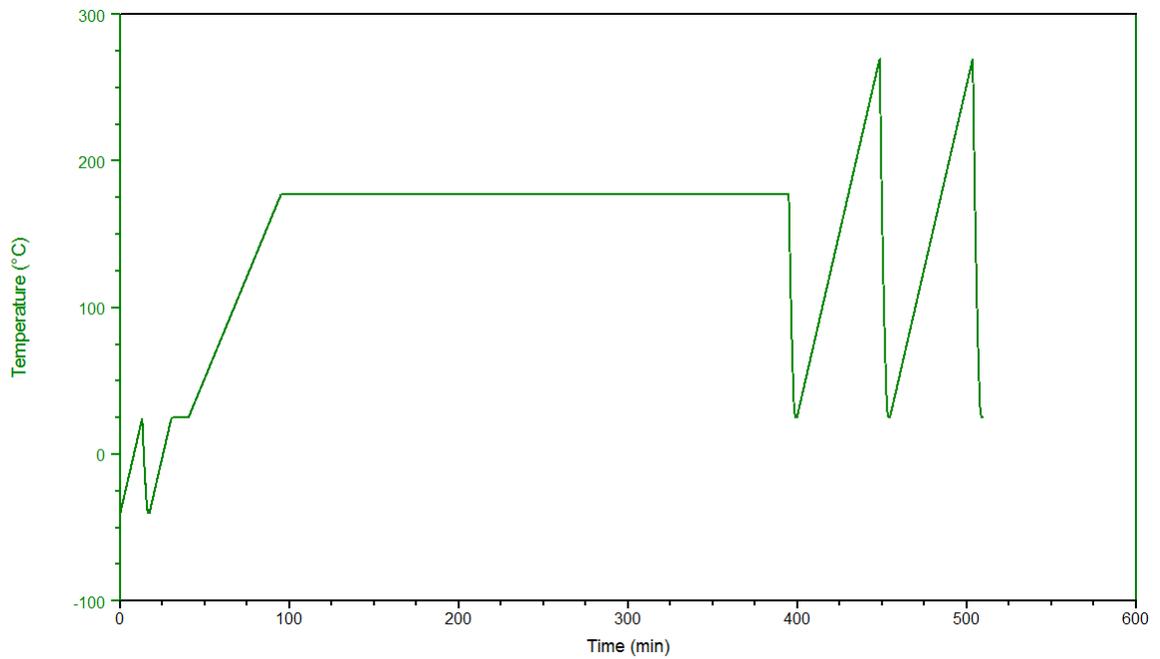


Figure 12. The DSC cure cycle used for curing 5320-8HS aged samples. The cure profiles includes sub-tg dynamic scan followed by a ramp rate to proceed to isothermal step.

### 3.4.1.4 IM7-8552 Autoclave Prepreg

Figure shows the cure cycle used to cure IM7-8552 autoclave resin system. The profile initiates with a dynamic scan in which the sample was cooled down to  $-40\text{ }^{\circ}\text{C}$  and heated up with  $5^{\circ}\text{C}/\text{min}$  rate to  $30\text{ }^{\circ}\text{C}$  to obtain the sub-ambient glass transition temperature. Then sample was heated to  $71\text{ }^{\circ}\text{C}$  by a  $1.1^{\circ}\text{C}/\text{min}$  rate and the temperature was maintained constant for 60 minutes. Then second ramp rate (same as first) was applied to proceed to the post cure temperature of  $126\text{ }^{\circ}\text{C}$ . The temperature was then maintained for 360 minutes to reach fully cured state. To obtain glass transition temperature and residual heat of reaction two dynamic scans were additionally performed at the end of cure cycle. This could increase the chance of consistency of the values obtained for Tg. Dynamic scan includes a fast ramp rate of  $5^{\circ}\text{C}/\text{min}$  rate to  $295\text{ }^{\circ}\text{C}$  during which the material changes to a rubbery state and Tg could be obtained.

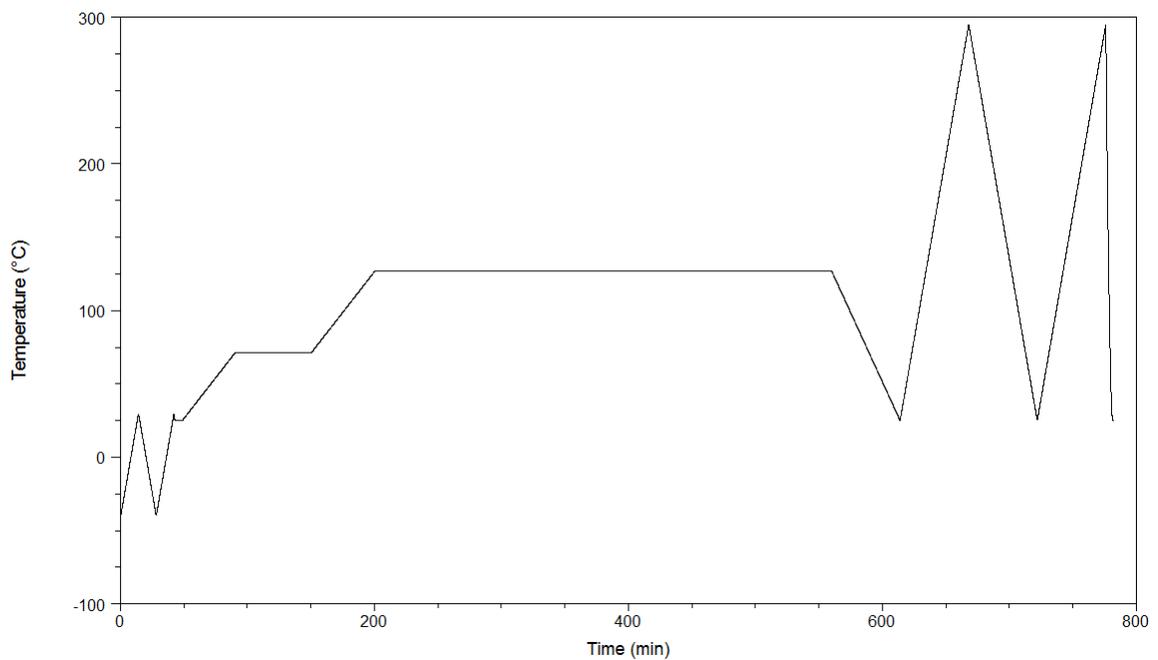


Figure 13. DSC cure profile for IM7-8552

### 3.4.2 DSC Measurements

In this subsection the basic DSC measurements that were utilized to characterize the cure process were represented. These experimental measurements were necessary to interpret the thermal transitions. The measurements of the heat of reaction, the extent of conversion, and of the Sub-ambient glass transition temperature were carried for different out-times.

Experimental measurements for thermal analysis were performed utilizing two-step and dynamic cure profiles. Moreover a good understanding of the state of reaction and response of material to out-time was obtained.

#### 3.4.2.1 Heat of Reaction

For thermosetting resin systems the cure process is an exothermic reaction in which the liquid resin turns into a glassy state solid. This enthalpy of this reaction is called the heat of reaction. As mentioned in previous chapter several methods have been proposed and discussed in the literature. In this work, the heat of reaction was calculated by integrating the area under the heat flow curves obtained from DSC. Fundamental to this goal is the methodology of detecting the baseline. In this study a linear baseline was used to integrate the area under the heat flow curve.

### 3.5 Rheology Analysis

Viscoelastic properties during cure play a vital role in the final mechanical properties of the composite laminates. Uncontrolled cure may cause undesired and excessive thermal and rheological variations that can induce microscopic and macroscopic defects in the composite part. In the present work a novel shear rheometry has been utilized to prove the ability of the material state management approach in prediction of material behavior.

#### 3.5.1 Shear Rheometer

“AvPro ADT CSS 2000” rheometer has been used to carry out rheology experiments to investigate out-time on the viscoelastic properties of 5320-8HS and IM7-8552. Viscoelastic properties of the mentioned prepreg resin systems were obtained using encapsulated shear testing on an AvPro ATD CSS 2000 rheometer for pristine as well as aged material. This rheometer is designed with two parallel plates of 41.3 mm diameter. Each plate has 20 grooves arranged in radial pattern to prevent the sample slippage at high torque. ADT is capable of generating reliable and consistent results. It can measure the viscoelastic properties of prepreg from the low viscosity region to the solid glassy region.

During the experiment, the ATD’ upper die moves down and encapsulates the sample between two parallel plates. Then the control system drives the motor to apply the programmed torque using a sinusoidal oscillation. The upper die is equipped with a transducer to measure the transmitted torque. This arrangement is called a control strain-stress system since the material response to applying deformation is measured using an input-output method. Figure 14 shows the arrangement of the motor, transducer, heater and sensor in upper and lower dies of ATD 2000.

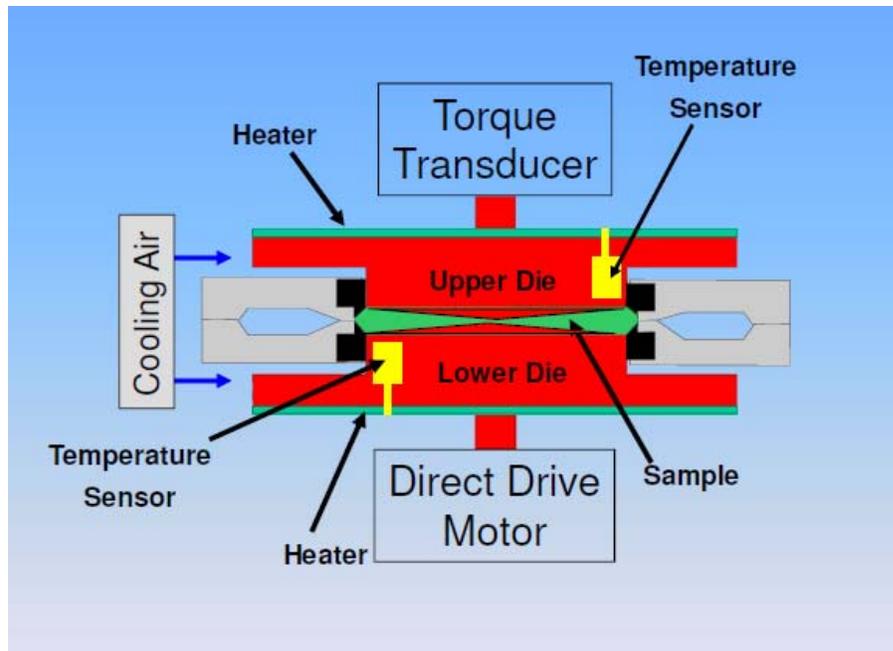


Figure 14. The arrangement of direct drive motor and transducer in ATD 2000

The transmitted deformation measured by the transducer is the complex modulus  $G^*$ . The shear complex modulus  $G^*$  consists of a real and an imaginary component representing the elastic and viscous nature of material. The elastic component (real number, in-phase with applied strain) is called storage modulus,  $G'$  and the viscous component (imaginary number, out-of-phase with applied strain) is called loss modulus  $G''$ .

### 3.5.1.1 Rheometer Samples

5320-8HS prepreg samples were prepared using 9 plies with a nominal cured thickness of 2.9 mm and an average weight of 5.5 gr. To prevent the bleeding during cure and to ease the removal of the sample after testing, all samples were tested with O-rings and Kapton films. Experiments were conducted at a strain of 0.05 degrees and a constant frequency of 1 Hz.

IM7-8552 prepreg samples consisting of 16 plies with a nominal cured thickness of 2.9 mm and constant weight of 6 gr were used in this study. Figure 15 shows a cured rheometer

sample. After preparation, all rheometer samples were stored out of the freezer inside plastic bag along with the desiccant to minimize the moisture effects at room temperature.



Figure 15.ATD shear rheometer cured sample.

#### 3.5.1.2 Rheometer Cure Profile

#### 3.5.1.3 5320-8HS Out-of-autoclave Prepreg

Overall two cure profiles were used for the out-time study of 5320-8HS, out-of-autoclave prepreg. The cure profiles varied in their heating ramp rates and are plotted against time in figure 16. The cure cycle initiates with a heating rate to reach the determined isothermal temperature. The temperature was constant for 120 minutes followed by a cool down rate. Although the prepreg sample was not fully cured at the end of cure cycle, the low viscosity region was reached. This cure cycle was aimed to focus on the minimum viscosity region and gelation for different out-times.

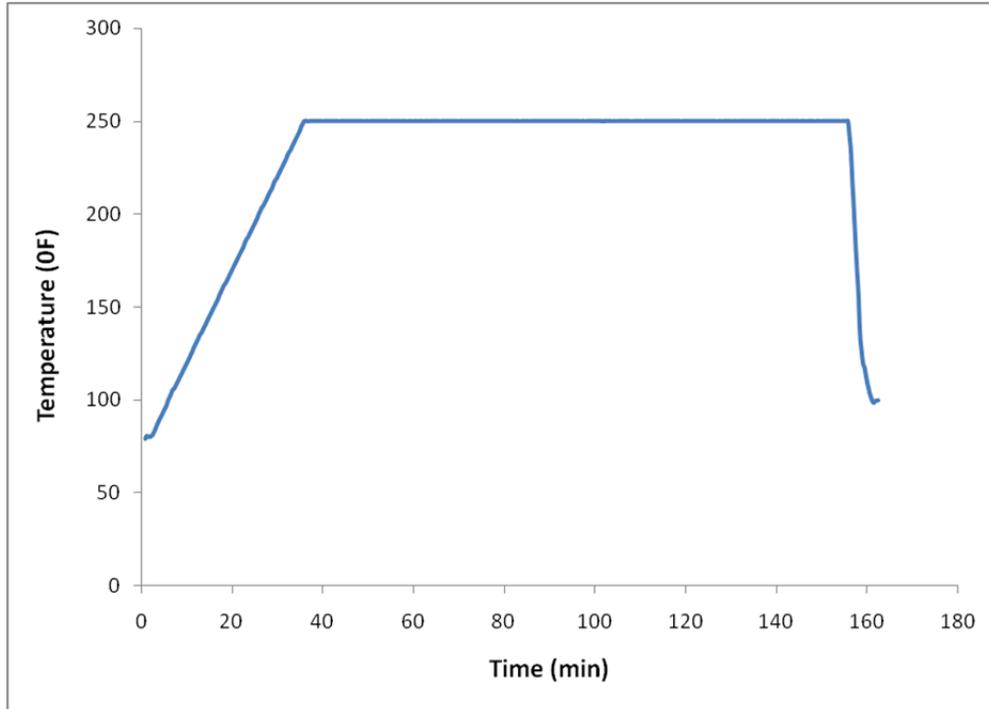


Figure 16. The rheometer cure cycle for 5320-8HS samples.

#### 3.5.1.4 IM7-8552 Autoclave Prepreg

Table 1 and Figure 17 show the cure profile used to study the effect of ambient aging on IM7-8552 autoclave prepreg. A two-step cure cycle recommended by the manufacturer was used by the shear rheometer to cure the prepreg samples. The first step, which is referred to as intermediate cure, is when an isothermal temperature of 71 °C applied to the sample for a dwell time of 60 minutes and then it proceeds to second step by heating ramp rate of 1.1 °C/min. The Second part, which is called post cure, is an isothermal temperature of 127 °C for a dwell time of 360 minutes and allows the sample to reach the fully cured state.

Table 1. Cure cycle for IM7-8552 aging study.

First ramp-Up (°C/min)	Intermediate cure temperature (°C)	Intermediate cure time (min)	Second ramp-Up (°C/min)	Post cure temperature (°C)	Post cure time (min)	Ramp-down (°C/min)
1.1	71	60	1.1	127	360	1.9

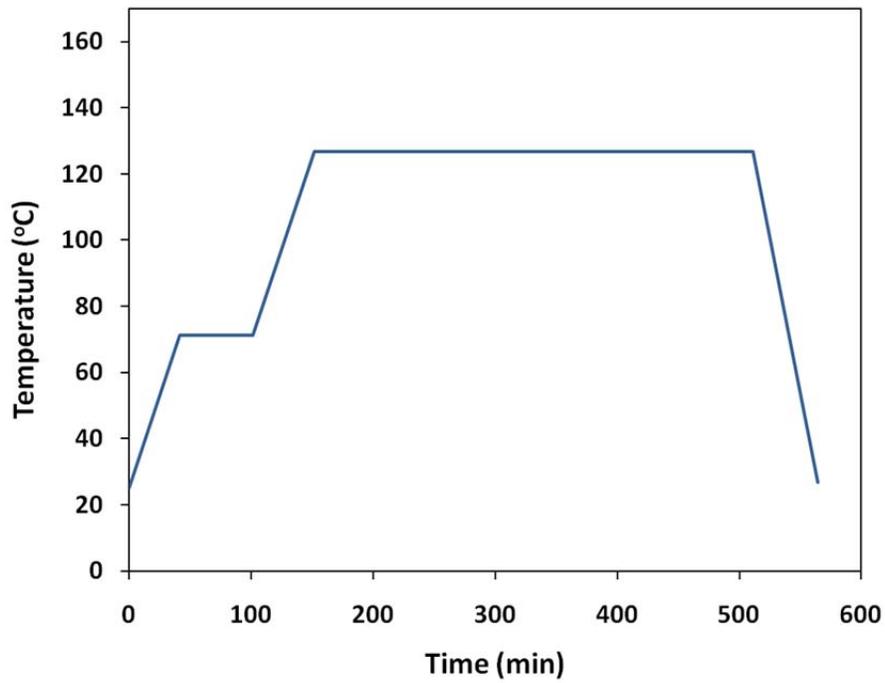


Figure 17. Cure cycle for IM7-8552 out-time study.

### 3.5.2 Rheological Measurements

To understand the state of the cure using the proposed approach, aged prepregs were tested every other day for a total of 40 days for IM7-8552. For 5320 resin 0, 10 and 18 days were proposed as aging increments. In this work the viscoelastic transitions during cure was monitored based on the following rheological properties obtained from the shear rheometer. Experimental tests were carried out based on ASTM standards which outline the important viscoelastic properties as:

- Shear Storage modulus  $G'$  (Elastic)
- Shear Loss modulus  $G''$  (Viscous)
- Complex viscosity  $\eta^*$
- Damping factor  $\tan \delta$

During the out-time study, minimum viscosity, gelation, vitrification and glass transition temperature were obtained for each sample using the viscoelastic properties of the prepreg during cure.

## CHAPTER 4

### RESULTS AND DISCUSSION

In this chapter, the experimental results from the out-time study are discussed. The result and discussion chapter includes the thermal and rheological analysis for out-of-autoclave and autoclave prepreg resin systems. For each subsection, multiple tests were performed using DSC and encapsulated Shear Rheometer to investigate the kinetics and rheology of prepreg during out-time.

#### 4.1 5320-8HS Out-of-autoclave Prepreg

##### 4.1.1 Rheological Analysis

The Science of Rheology has been of great importance in the processing of polymeric composites since the knowledge of Rheology, helps the design engineers overcome the shortcomings of the traditional time-temperature approach. Utilizing viscoelastic properties such as dynamic shear moduli,  $G'$  and  $G''$  a good understanding of the transitions and reactions during cure can be obtained. Basically prepreg processability and its final properties after cure depend on the transitional events during cure such as minimum viscosity, gel point and verification. Figure 18 illustrates how these transitions were obtained based on their viscoelastic properties using plot versus time

In this study, viscoelastic properties of prepreps such as storage modulus, loss modulus and damping factor were obtained to characterize the material behavior during out-time. To investigate more all of the experimental results were plotted against curing time and presented in this chapter. For 5320-8HS rheology experiments were carried out for 0, 10 and 18 out-time. The 0-day material was assumed to be pristine.

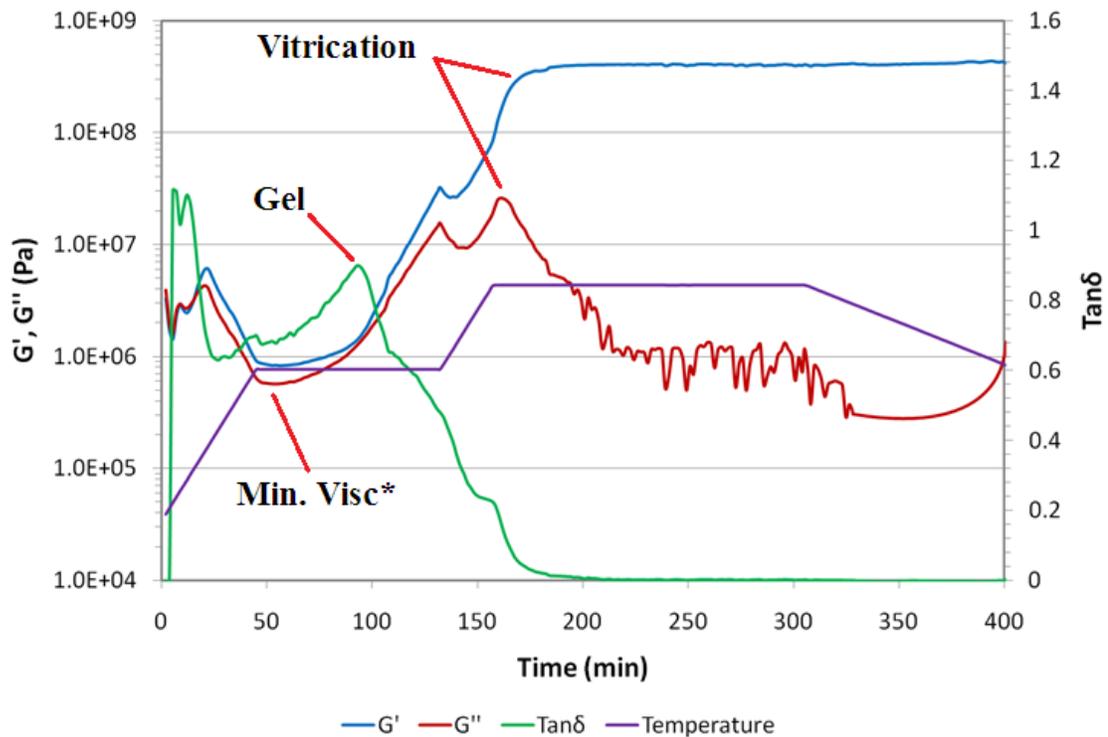


Figure 18. Viscoelastic transitional events during cure.

The main goal of this work was to evaluate the processability of the prepreg based on its viscoelastic properties. This study was based on some issues associated with some batches of 5320-8HS supplied to manufacturing destination. The main problem was the void content of manufactured parts which did not satisfy the standards requirement. To address this issue the suspect batch was evaluated using the proposed approach. A large number of experiments utilizing shear rheometer were performed

#### 4.1.1.1 Pristine Material (0-day prepreg)

Figure 19-20 illustrates the viscoelastic properties for the pristine 5320-8HS prepreg versus cure time for two different cure cycles. The cure cycles were varied in their initial ramp rate and aimed for comparing the effect of ramp rate on viscoelastic properties during out-time.

The plots clearly show the minimum viscosity, gel point and vitrification point for 0-day using two different ramp rates. Figure 10 shows the storage modulus, loss modulus, Tan delta and complex viscosity for a sample cured with a faster rate of 2.7 C/min. On the other hand the viscoelastic properties of the pristine sample cured with a lower ramp rate was plotted in Figure 19. Two variables were studied in this experiment including prepreg out-time and ramp rate. The variation of ramp rate did not change the shape of the curve but it did shift the complex viscosity, storage modulus,  $G'$ , and  $\tan \delta$  curves to the left.

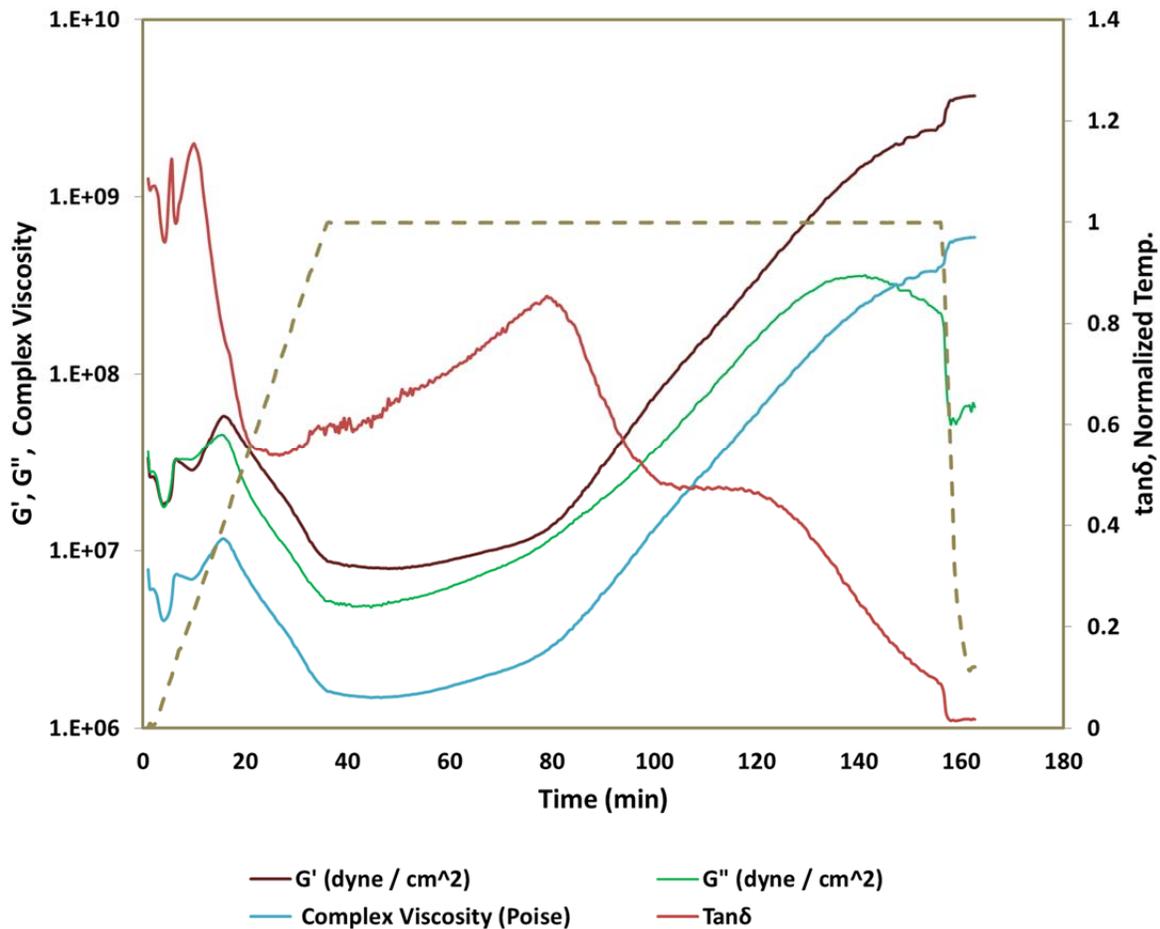


Figure 19. Viscoelastic properties of pristine 5320-8HS prepreg cured with 2.7 C/min ramp rate

As expected the experimental results for complex viscosity show that the higher ramp

rate results in lower cure time. It was also observed that the first sample (cured with higher ramp) reached gel point after 40 minutes while for the second sample, it took 180 minutes to reach the gel point.

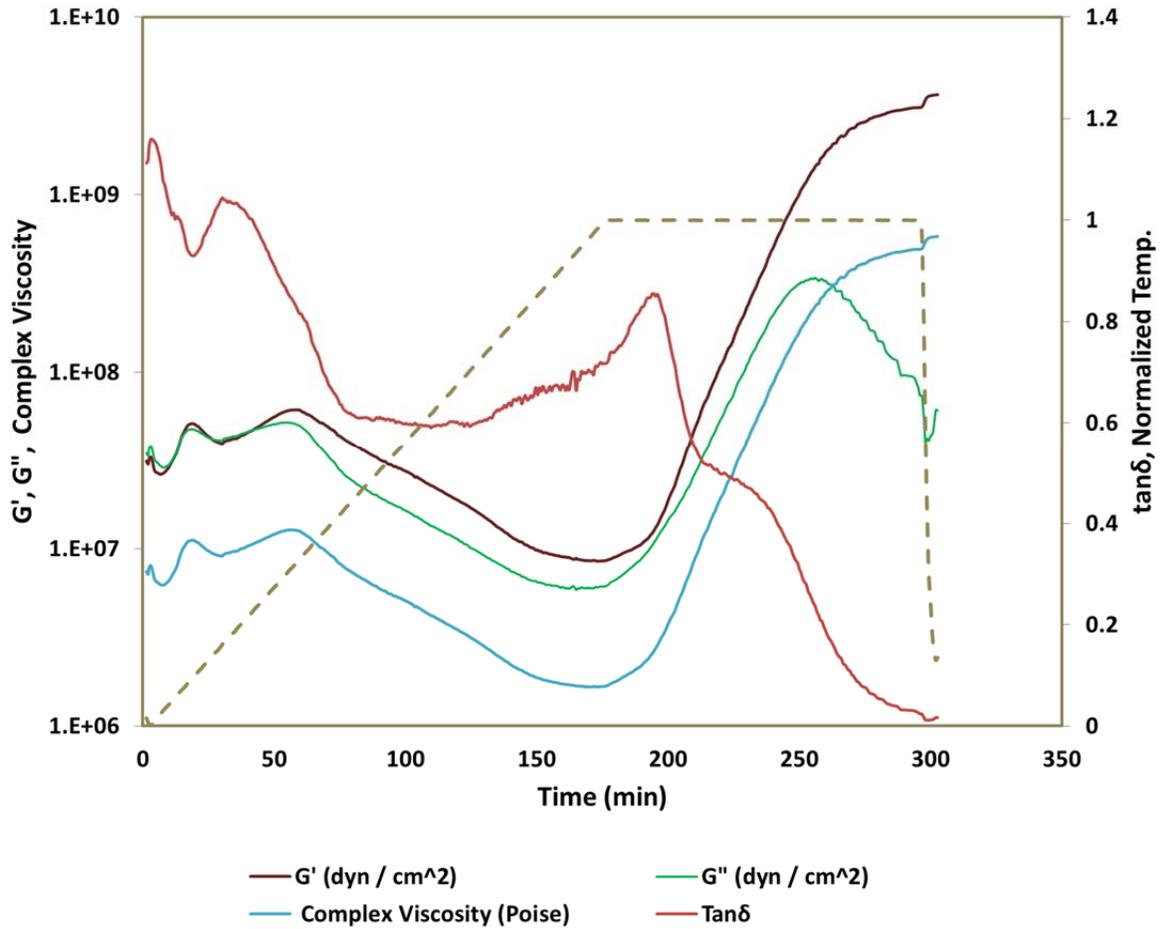


Figure 20. Viscoelastic properties of pristine 5320-8HS prepreg cured with 0.54 C/min ramp rate

Although the cure cycle was not meant to reach vitrification, for the slower cure cycle the isothermal temperature was held longer to achieve the fully cured state. Although the vitrification does not indicate the end of the network formation, it marks that glass transition temperature has become equal to cure temperature.

#### 4.1.1.2 Complex Viscosity

As mentioned, the complex viscosity plays a main role in the processing of prepregs due to the viscoelastic nature of the resin. Thus tracking of the minimum viscosity region has been the focus of this study. Figure 21 shows the complex viscosity and damping factor against curing time for 0, 10 and 18 days out-time. The experimental results show an upward shift in the complex viscosity as the material advanced to aging. In contrast to the whole increasing trend, the minimum viscosity value for day-10 is even less than day-0 which was expected to be higher due to the advancement in aging. However, the minimum viscosity value for day-18 was increased and got back to the expected trend. when the material is kept out-side of its storage environment under ambient temperature for lay-up or any other purpose, the cure advancement begins even though the reaction rate is slow, as a result the viscosity is expected to increase.

Unlike the minimum viscosity, the gel time was decreased with out-time and it showed a good trend with respect to out-time. The gelation time was observed to decrease from a value of 80 minutes for day-0 to a value of 50 minutes for 18-day.

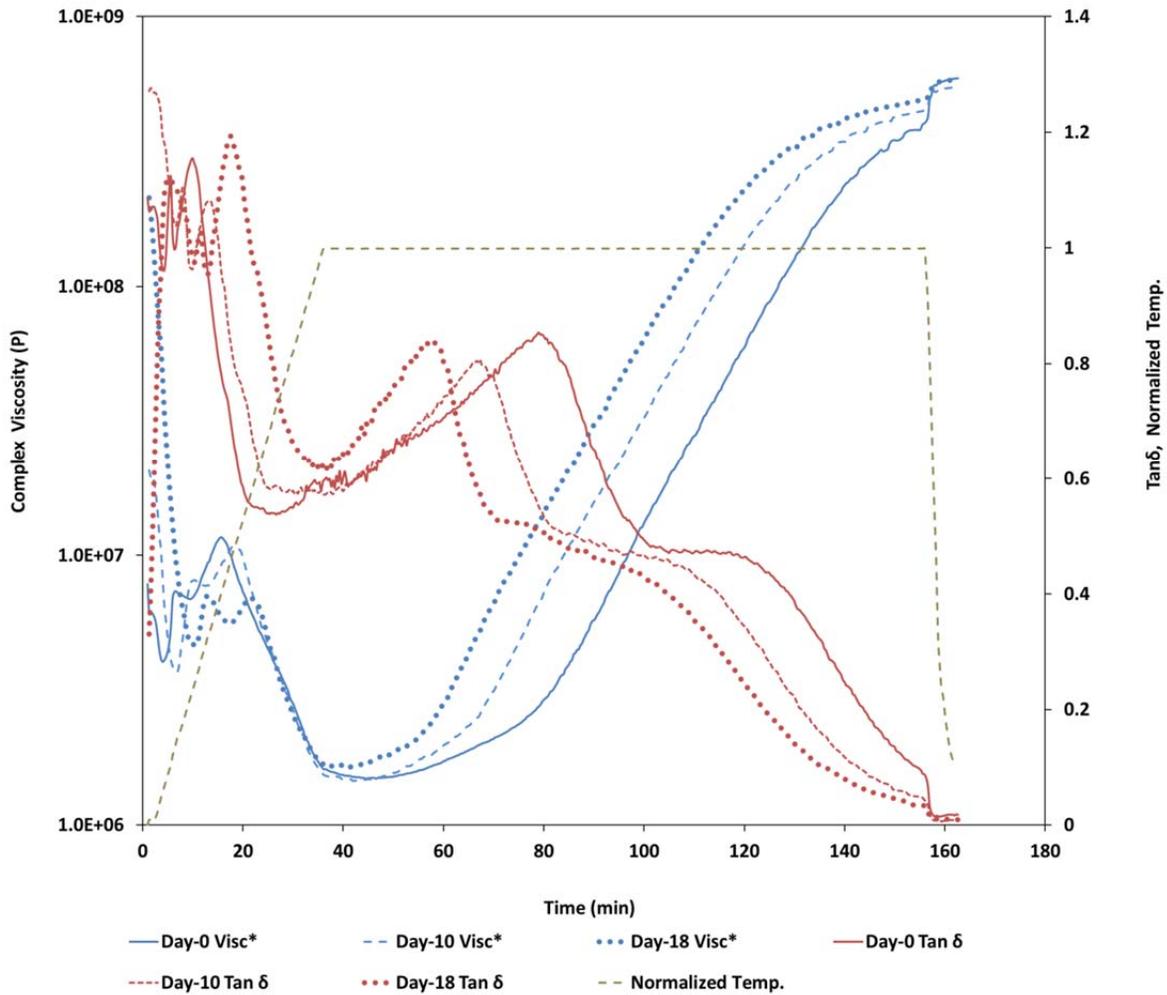


Figure 21. Complex viscosity versus time for day-0, day-10 and day-18,

This unusual behavior of the day-10 prepreg sample raised technical questions and the posed a serious questions about the quality of resin which will be discussed later in this chapter.

## 4.1.2 Thermal Analysis

### 4.1.2.1 Heat Flow

Figure 22 shows the change in heat flow curves for different out-times of 5320-8HS prepreg samples. The shift in the heat flow curve illustrates the effects of premature advancement of cure on cure kinetics of prepreg. To characterize the thermal behavior of the out-of-autoclave prepreg during out-time, heat flow data has been used to calculate parameters such as total heat of reaction, degree of cure, and residual heat of reaction. Furthermore the calculated values were plotted versus out-time to fully understand the trend of prepreg.

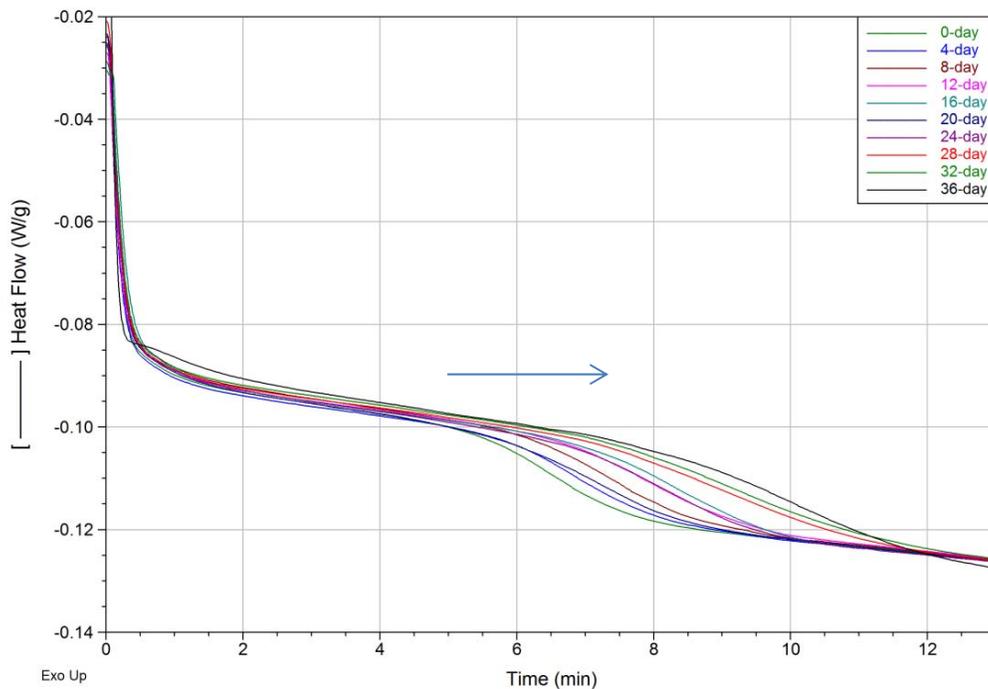


Figure 22: The shift in heat flow curve at sub-ambient temperature for aged prepreg.

#### 4.1.2.2 Sub-ambient Glass Transition Temperature (Sub-Tg)

Sub-ambient glass transition temperature, sub-Tg, is a temperature at which the uncured prepreg changes from a solid, frozen state to a rubbery state. Sub-Tg has been a very effective method in determining out-time of prepreg [56]. By running a temperature sweep test, sub-Tg can be determined from the heat-flow curve that is obtained from DSC. It shows that the heat flow curve shifts as the material advances in aging. Figure 23 shows the typical method used for obtaining sub-Tg from heat flow curve. To obtain the sub-Tg the sample was equilibrated at  $-40^{\circ}\text{C}$ , followed by a ramp up rate of  $5^{\circ}\text{C}/\text{min}$  up to  $30^{\circ}\text{C}$ . For out-times ranging from 0-day to 40-day, as illustrated in Figure 24, a linearly increasing trend was obtained for the sub-Tg with respect to out-time. With the observed  $R^2 = 0.99$ , sub-Tg test is presenting a strong correlation with out-time and could be one of the most effective methods in determining prepreg out-time.

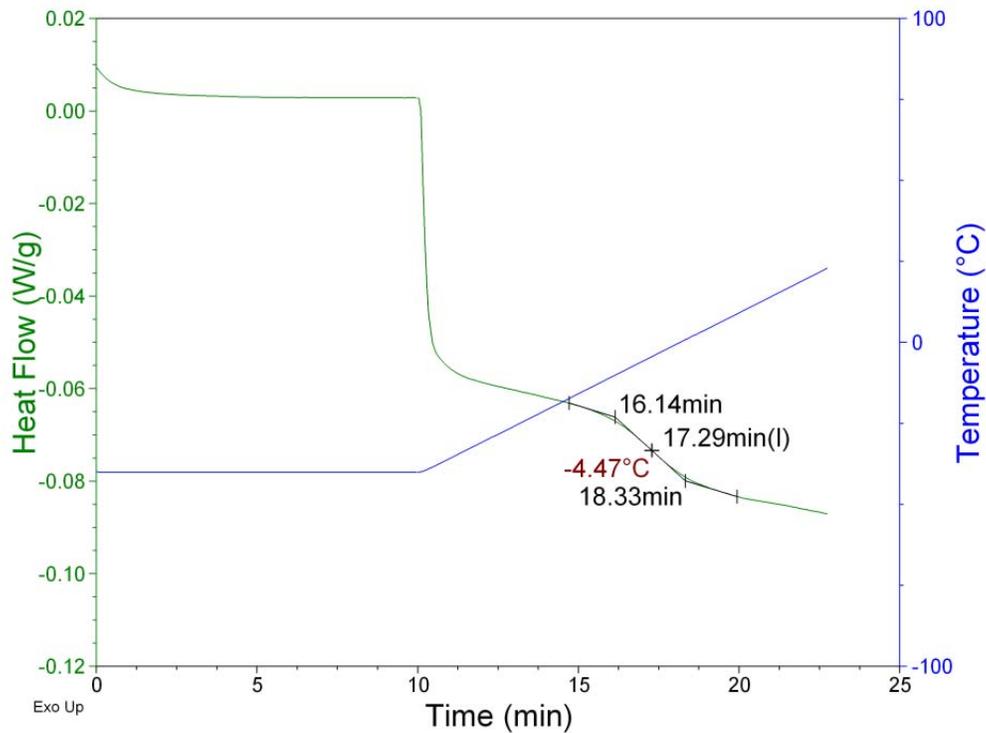


Figure 23. The typical method used to obtain sub-ambient Tg.

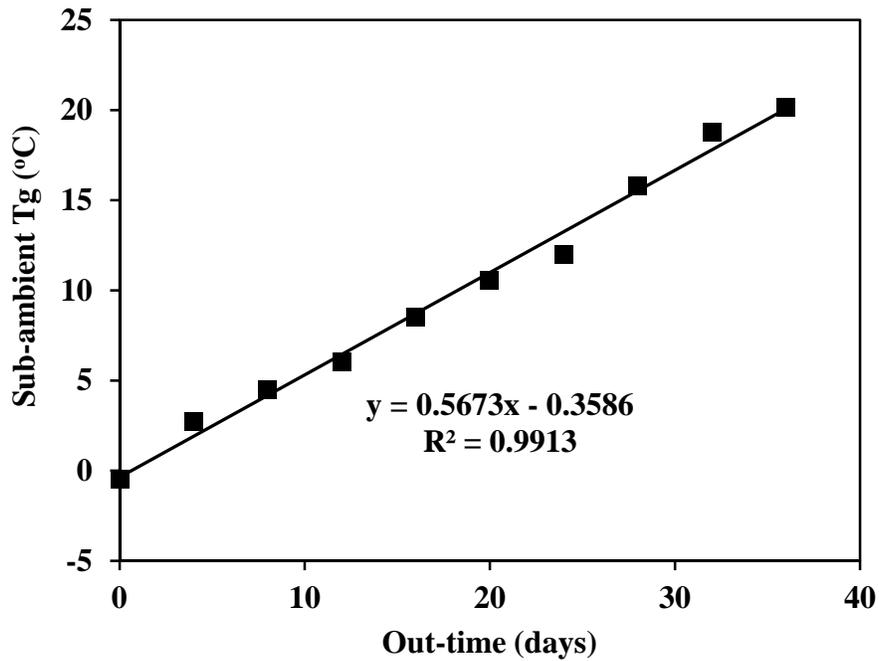


Figure 24. The sub-ambient Tg versus out-time for 5320-8HS.

#### 4.1.2.3 Heat of Reaction

Measuring the degree of cure for different out-times was performed to track the behavior of material over out-time. The total heat of reaction is defined as the total heat released during an exothermic cure process. Figure 25 illustrates the typical method used to calculate the total heat of reaction and peak temperature by using a dynamic temperature scan. As shown a linear baseline was used to integrate the area under exothermic heat flow curve.

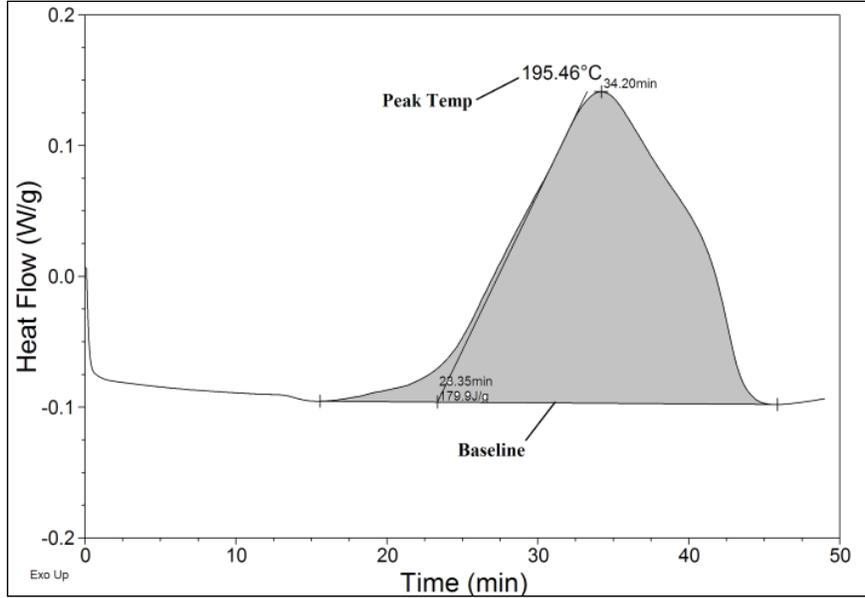


Figure 25. The heat of reaction and peak temperature for the pristine sample.

To study the out-time effect on cure kinetics, the heat of reaction for different out-times was calculated based on the heat flow obtained from the dynamic DSC scan, using the following equation:

$$H_{cure,T} = \int \left( \frac{dH}{dt} \right) dt \quad (28)$$

Where  $H_{cure,T}$  is the heat of reaction for different out-time days (T) obtained by integrating the change in heat flow ( $dH/dt$ ) during the reaction time (t) (Figure 25). From equation (28),  $H_{cure,T}$  was calculated from the heat flow curve using a sigmoidal horizontal baseline and is plotted in Figure 26. A linearly decreasing trend in the total heat of reaction was observed as the material advanced in aging. As such, the total heat of reaction can also be used to determine out-time of the aged prepreg.

To obtain the heat of reaction for different out-times, it was assumed that the ultimate heat of reaction  $H_{Ultimate}$  remained constant with the aging of the material and was equal to  $H_{Cure,0}$

of the 0-day sample ( $H_{Ultimate} = H_{Cure,0}$ ). The heat of reaction during out-time T,  $H_{aging,T}$  can be calculated by using the following relationship:

$$H_{Ultimate} = H_{Aging,T} + H_{Cure,T} \quad (29)$$

Figure 27 shows the heat of reaction due to material aging for different out-times. Similar to sub-Tg,  $H_{Aging,T}$  was increasing with respect to out-time. A linearly increasing trend was observed for  $H_{Aging,T}$ , with increasing out-times up to 40 days.

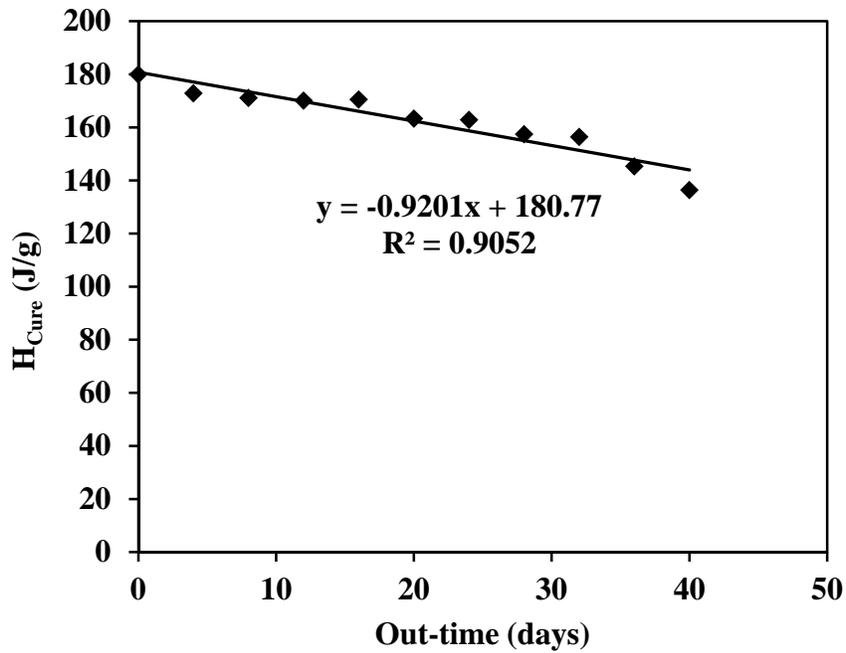


Figure 26. The heat of reaction for different out-times.

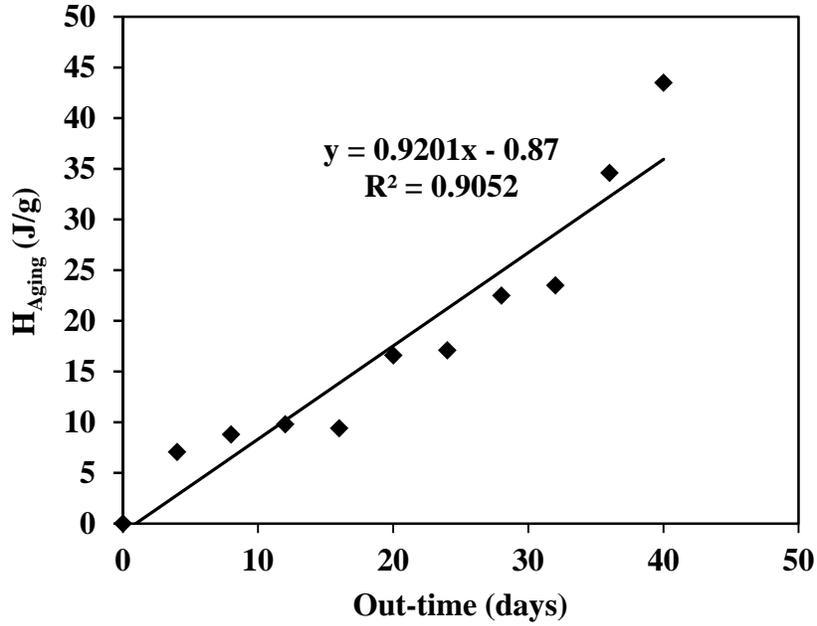


Figure 27. The heat of reaction due to aging,  $H_{Aging}$  versus out-time.

#### 4.1.2.4 Degree of Cure

By using the above heat of reactions, the relationship between the kinetic reaction and out-time can be drawn using cure conversion. The degree of cure for different aged samples can be determined by:

$$\alpha_{Cure,T}(t) = \frac{1}{H_U} \int \left( \frac{dH}{dt} \right) dt \quad (30)$$

Where  $\alpha_{Cure,T}$ , is the degree of cure for different out-times T. Additionally, using equation (29), the percent of conversion due to aging,  $\alpha_{Aging,T}$  of the material due to out-time T, can be defined as:

$$\alpha_{Aging,T} = \frac{H_{Ultimate} - H_{Cure,T}}{H_{Ultimate}} = 1 - \frac{H_{Cure,T}}{H_{Ultimate}} \quad (31)$$

Figure 28-29 show the degree of conversion due to curing and aging, respectively, for different out-times. In this study, the 0-day out-time sample was assumed pristine for which  $\alpha_{Aging,0} = 0$ . Similar to  $H_{Cure}$  and  $H_{Aging}$ ,  $\alpha_{Cure}$  shows a linearly decreasing trend while  $\alpha_{Aging}$  shows a linearly increasing trend with increased out-time up to 40 days.

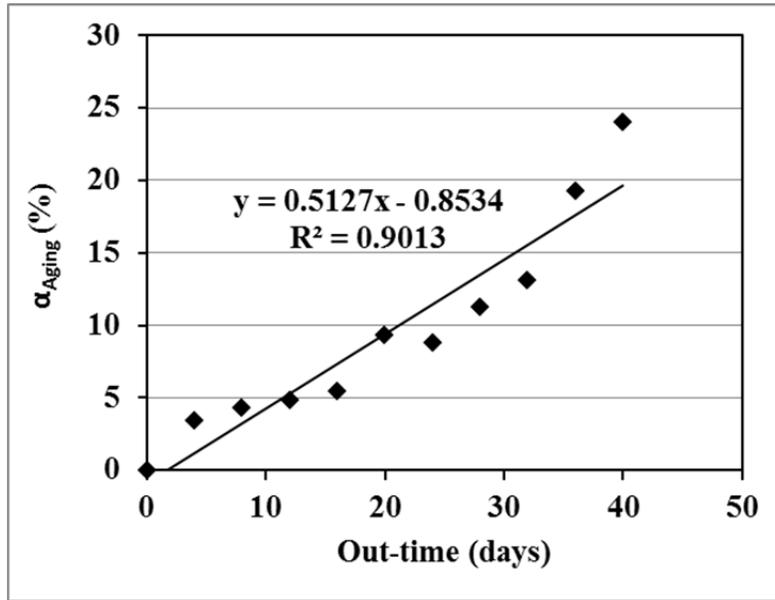


Figure 28. Degree of cure due to aging versus out-time (days). A Linear trend was observed for  $\alpha_{Aging}$  as the material advanced to aging.

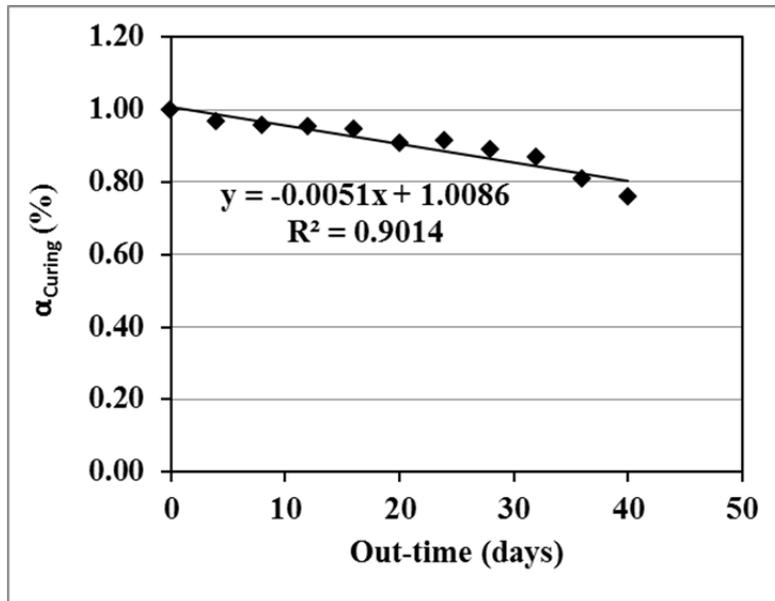


Figure 29. Final degree of cure obtained from DSC.

From equation (30), the degree of cure and rate of cure during cure for different out-time samples were calculated. Figure 30 shows the shift for degree of cure and rate of cure during cure for different out-time, respectively. It shows that the kinetic reaction progress decreases with the out time of the prepreg. This also indicates that the expired material may achieve the equivalent quality compared to unexpired material with a modified cure cycle.

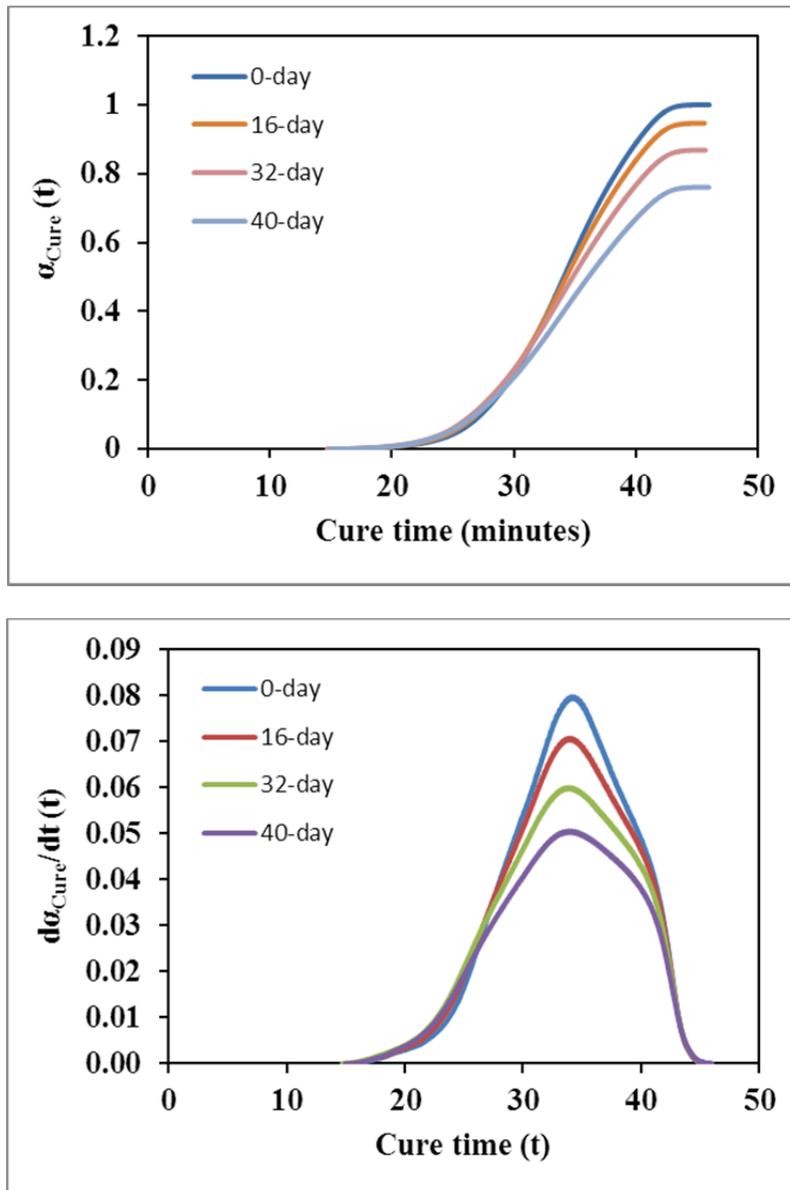


Figure 30. The shift in the degree of cure and rate of cure for different out-times.

#### 4.1.2.5 Activation Energy

The activation energy is a valuable tool in understanding the chemical reactions and mechanisms governing the cure process. The activation energy is a time- temperature shift factor which is useful in modeling the behavior of thermosets. In this work using Borchardt and Daniel's kinetic approach and per ASTM E698-05 [60], activation energy ( $E_a$ ) was obtained for different out-times and was plotted in Figure 31. The observation from  $E_a$  shows a linearly decreasing trend with the advancement of material to aging. This decreasing trend implies that considerable conversions are occurring at room temperature.

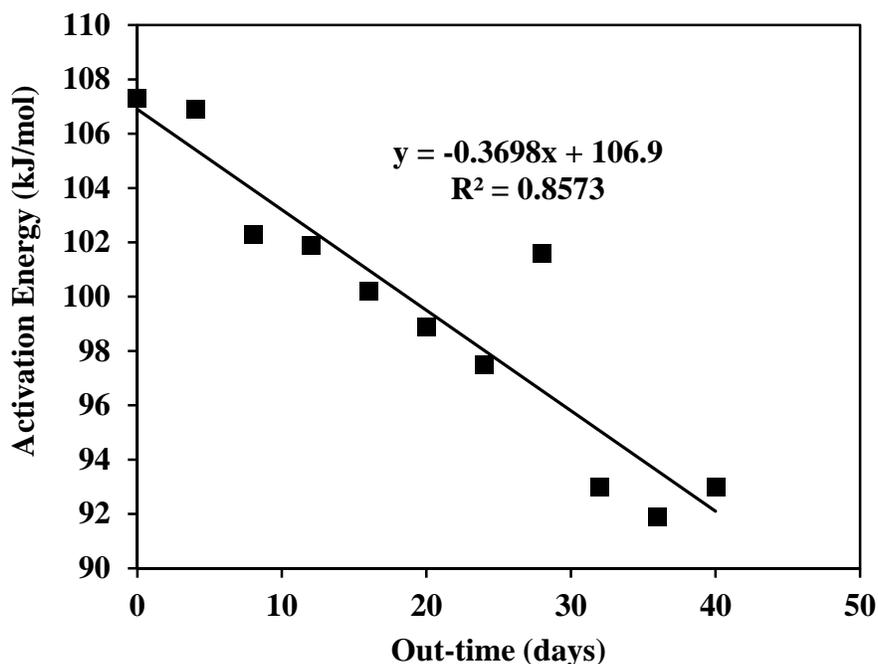


Figure 31. Activation energy versus out-time.

#### 4.1.2.6 Peak Temperature

In the study of cure kinetics, peak temperature is a parameter that represents the point where the maximum rate of cure occurs [61] and varies in a predictable manner with heating rate

[39]. Sakaguchi showed the resins cured at the lower peak exotherm temperature have decreased degrees of cure [62]. The peak temperature values are plotted for different out-times in Figure 32. The decreasing trend is an indication of a lower degree of cure for the aged material and the premature advancement of cure. The fluctuation in the data may be due to the minimal data points for each out-time.

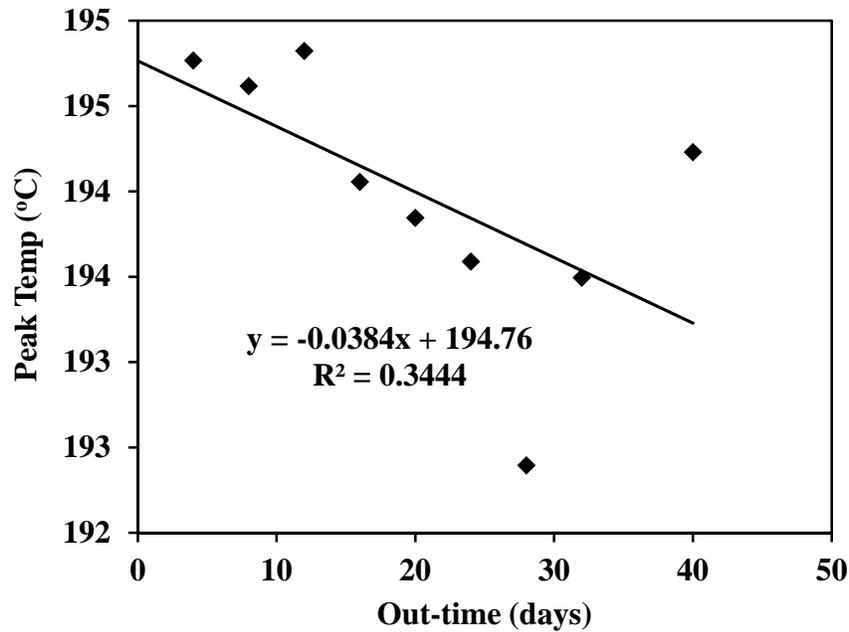


Figure 32. Peak temperature versus out-time.

#### 4.2 Hexcel IM7-8552 Out-of-autoclave Prepreg

Autoclave prepregs are being used as the main material for primary structures in the aerospace industry. Hexcel IM7-8552 is an amine cured; toughened epoxy resin system supplied with woven carbon fibers. It is a high performance tough epoxy matrix with an out-life of 21 days at room temperature. It exhibits good impact resistance and damage tolerance for a wide range of applications [3].

## 4.2.1 Rheological Analysis

### 4.2.1.1 Storage Modulus

Figure 33 demonstrates the storage modulus versus curing times for different out-times up to 40 days. As shown the advancement of the prepreg under ambient aging results in increasing the value of storage modulus. There is a significant increase in the minimum value of  $G'$  which is close to gel point. However the maximum value of  $G'$  is independent of out-time. Although the peak of storage modulus occurs sooner for aged samples, the plateau value is the same for different out-time. This may be attributed to the vitrification point that was reached due to cross linking.

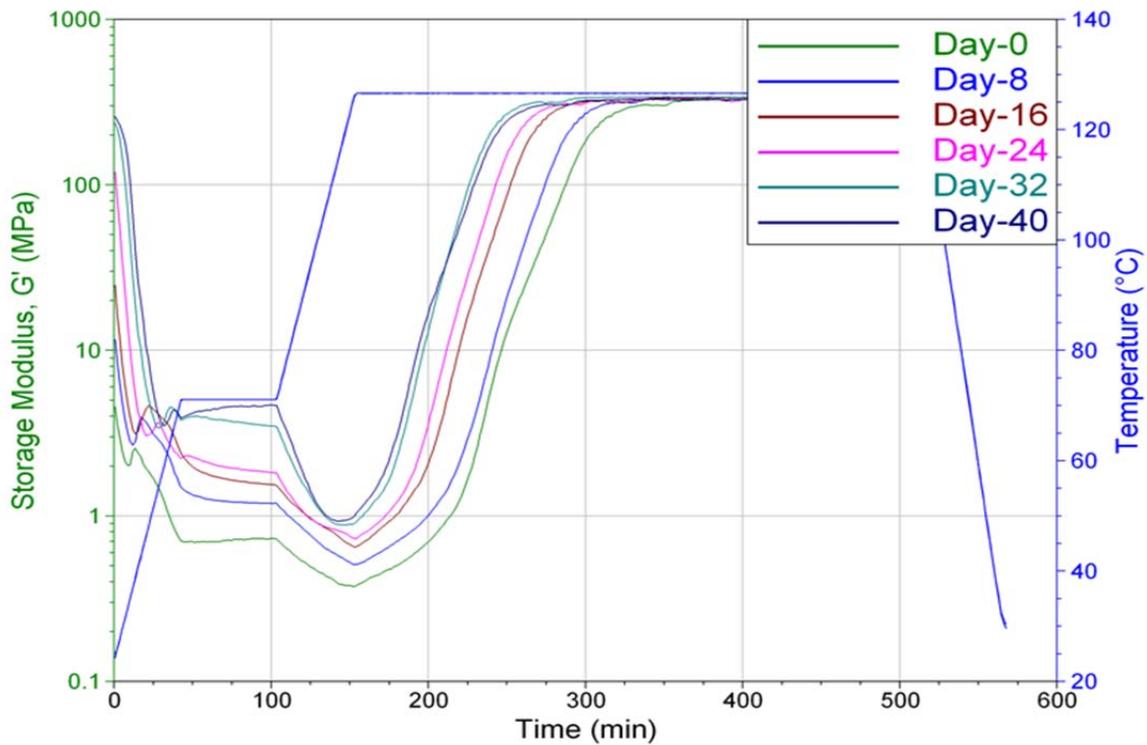


Figure 33. Storage modulus,  $G'$  versus time for different out-time

#### 4.2.1.2 Loss Modulus

The loss modulus was obtained for different out-times using the two-step cure profile. Figure 34 shows the loss modulus against curing time. Experimental results for the loss modulus show that the maximum value of the  $G''$  shifts to the left as the prepreg advances in aging. The tracking of loss modulus during out-time is of great importance since some methods identify the vitrification point as the peak of loss modulus. Therefore the shift in the peak of loss modulus will reveal the fact that the vitrification time is decreasing with respect to out-time. Additionally the maximum values of loss modulus were observed to decrease with respect to out-time. One reason for the maximum values of loss modulus was the premature advancement of cure under the ambient temperature.

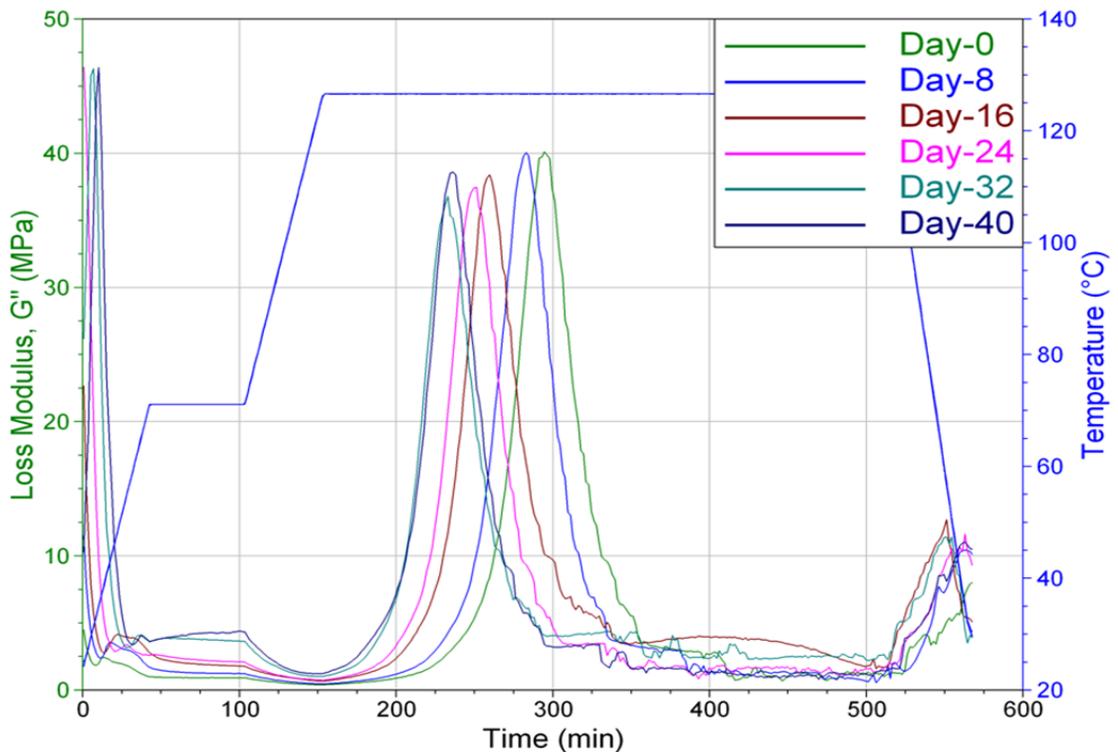


Figure 34. Loss modulus,  $G''$  against curing time for different out-time.

#### 4.2.1.3 Damping Factor

Figure 35 shows  $\tan \delta$  versus time for out-times up to 40 days.  $\tan \delta$  is the tangent of the phase lag between the dynamic stress and the strain and was obtained from the storage modulus and loss modulus.  $\tan \delta$  is a critical parameter in the processing of the prepreg since the gel time is defined to be the peak of the damping factor,  $\tan \delta$ , when the complex viscosity tends to be infinite. The plot shows a significant shift in the damping factor as the prepreg advances in aging from 0 to 40 days. Also the maximum value of  $\tan \delta$  was decreased with out-time. The shift in the damping factor plot to the left implies the lower gel time values for aged prepreg.

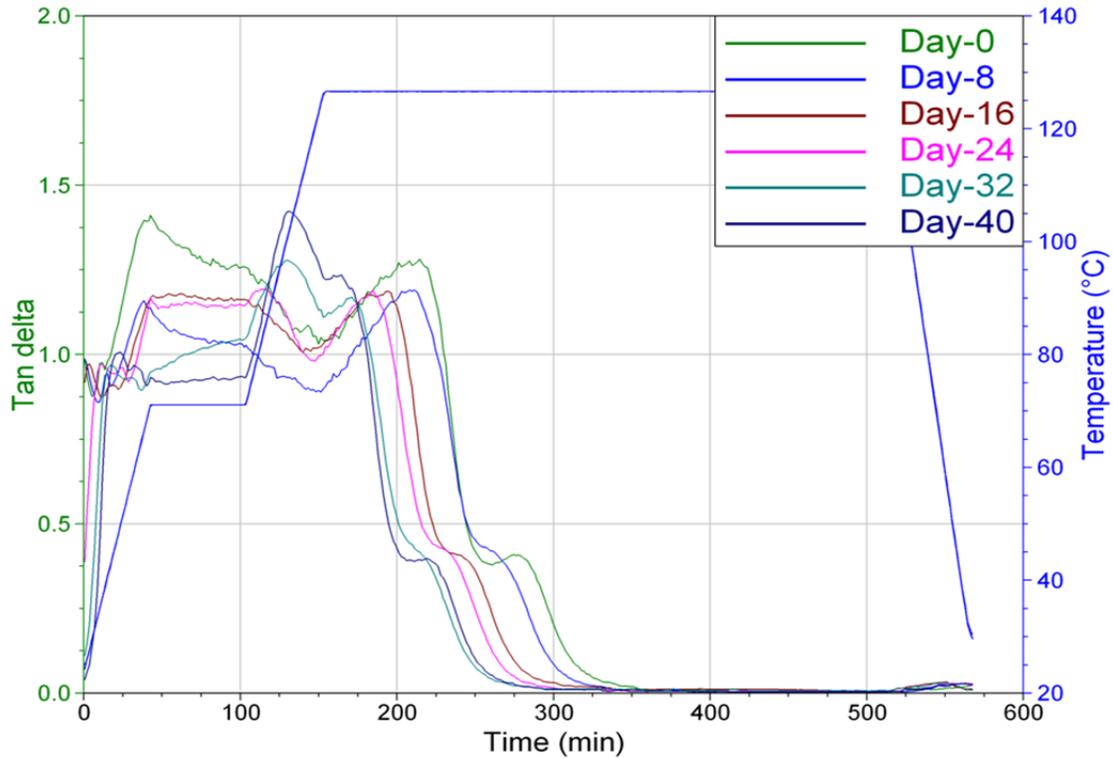


Figure 35. Damping factor for different out-times plotted against curing time.

#### 4.2.1.4 Complex Viscosity

As shown in Figure 36, the advancement of prepreg under ambient aging leads to an increase in complex viscosity. In this study, more emphasis is put on minimum viscosity since it is more vulnerable to the final mechanical properties of the laminate. The increase in viscosity during aging implies the decrease in mobility of the molecules and hence shows their limitation to flow and wet the fibers completely. The upward shift of complex viscosity implies the increase in the minimum viscosity and is an indication of cure advancement. This might cause several problems since premature advancement prior to process could cause poor consolidation and formation of voids through the thickness of laminate. Although the complex viscosity reaches its maximum value sooner for aged samples, the final plateau value does not vary and is independent of out-time.

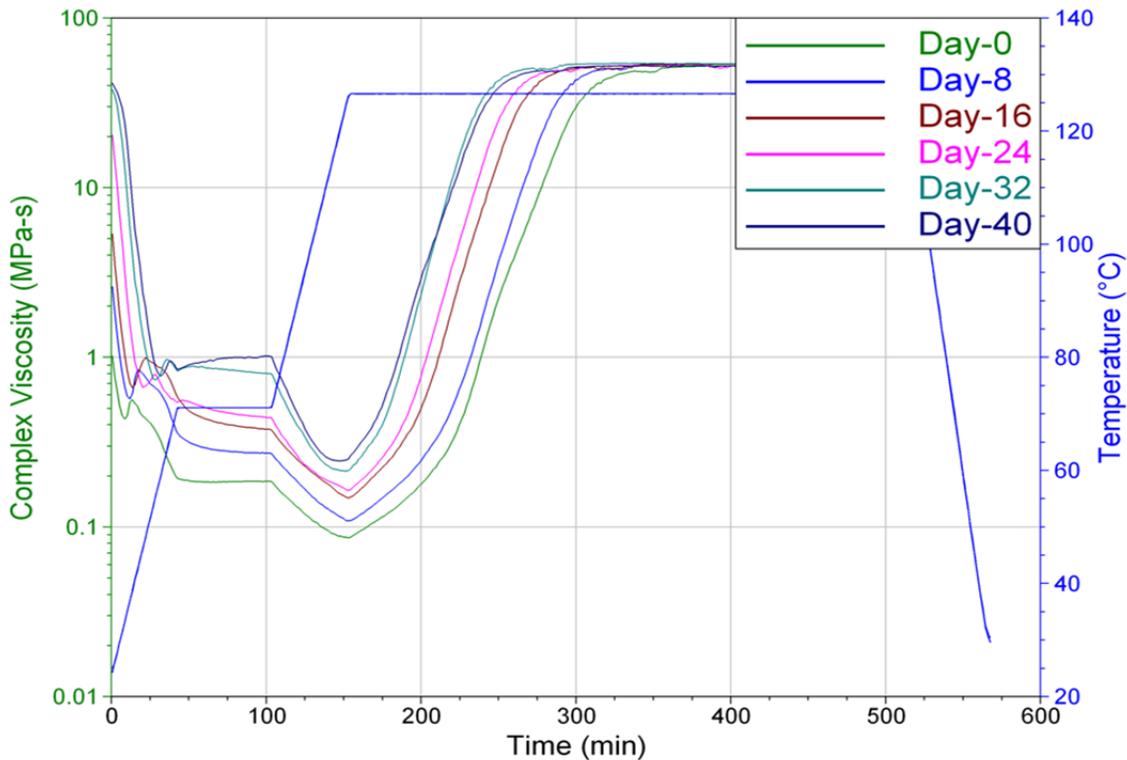


Figure 36. Damping factor for different out-times plotted against curing time.

#### 4.2.1.5 Minimum Viscosity

The minimum viscosity represents the time and temperature range during which resistance to flow has its lowest value. Resin viscosity during cure is a key parameter in the prediction of material behavior. Moreover, a good understanding of minimum viscosity region is critical in the processing of the prepreg. Technically, in the curing of prepreg, the resin infusion process is utilized. The resin viscosity must be low enough to wet and infuse uniformly around the fibers. After infusion, the resin viscosity must be high enough to prevent excessive bleeding due to trapped gases forcing the resin away from the fibers as the part is heated or the laminate is compressed to consolidate the layers. The time interval during which the resin flow is possible and viscosity is at or near its minimum value constitutes the processing window for resin infusion, gas removal and consolidation.

Figure 37-38 show the minimum viscosity and the minimum viscosity time versus out-time. As shown experimental results represent an increasing trend for minimum viscosity versus out-time. However, no significant change is observed in minimum viscosity time even for 40 days out-time. The stability of the minimum viscosity time reveals that

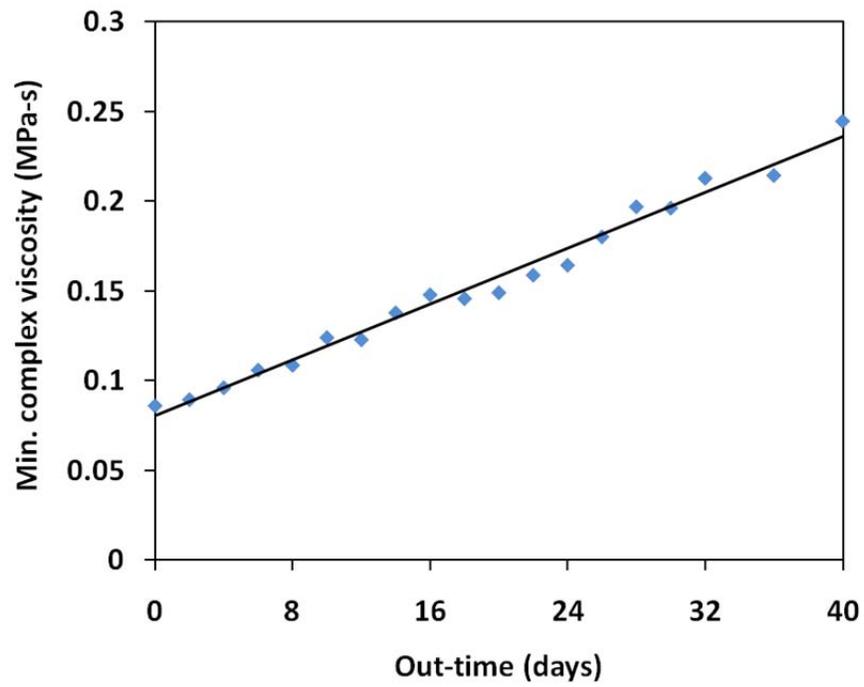


Figure 37. The minimum complex viscosity for different out-time.

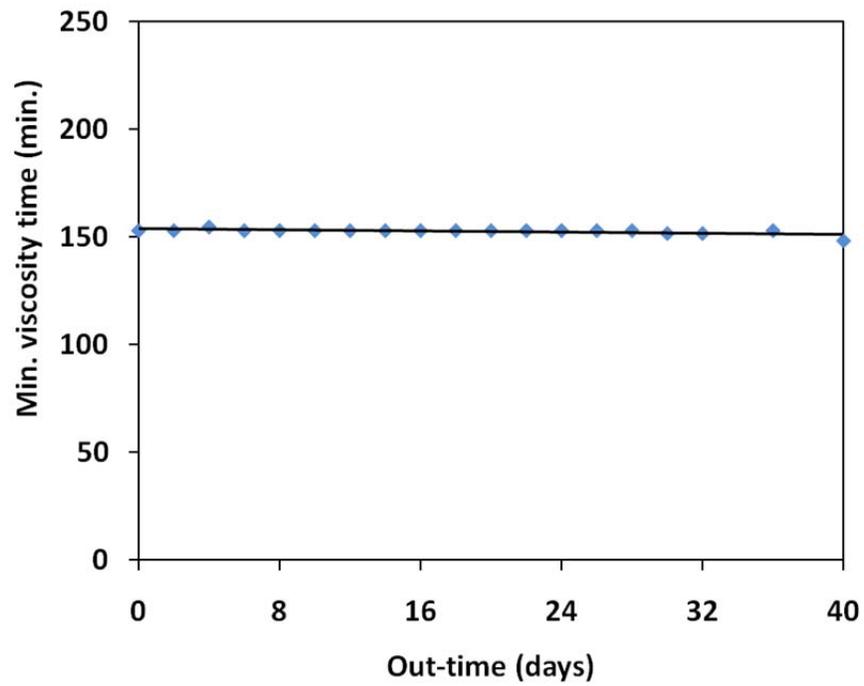


Figure 38. The minimum complex viscosity for different out-time.

#### 4.2.1.6 Gel Time

Gel time is an important transition during the cure process of thermoset resin systems. It is defined as the amount of time it takes for the prepreg to turn into a gel. Technically the gel point is reached when cross-linking starts to be dominant in the composite structure. Figure 39 shows the gel time versus out-time for IM7-8552. In this work the gel time was monitored since removing the trapped gaseous after gel point is almost impossible. This could cause several defects in the cured part. As shown, the advancement of material to aging leads to lower gel time for out-times up to 40 days.

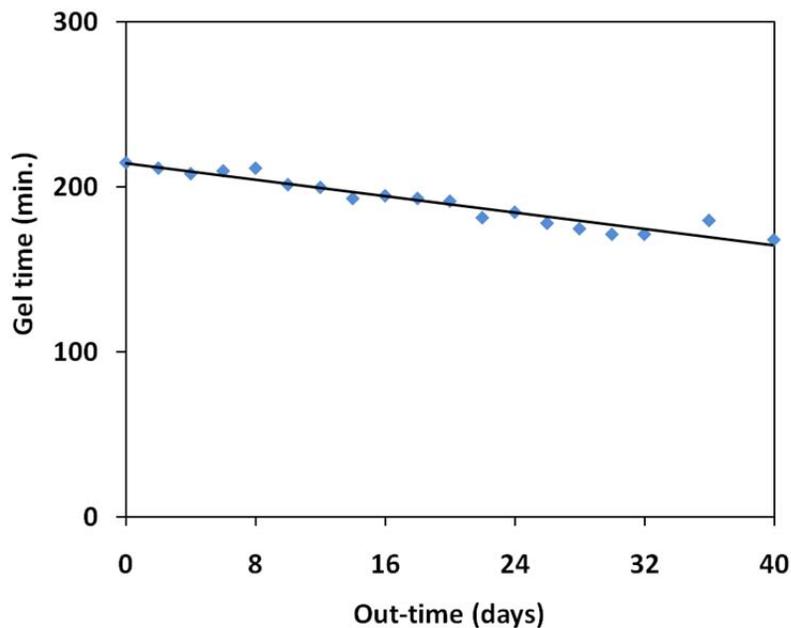


Figure 39. The gel time versus out-time (days)

#### 4.2.1.7 Vitrification

Vitrification time can be obtained utilizing different methods. Basically, at vitrification point the cure reaction changes diffusion controlled. In this work the time in which the storage

modulus reaches its plateau value was defined as the vitrification point. Figure 40 demonstrates the time of verification against out-time. Results show a decreasing trend for the verification time as the material advances to aging. This indicates that the cure reactions are occurring under an ambient temperature.

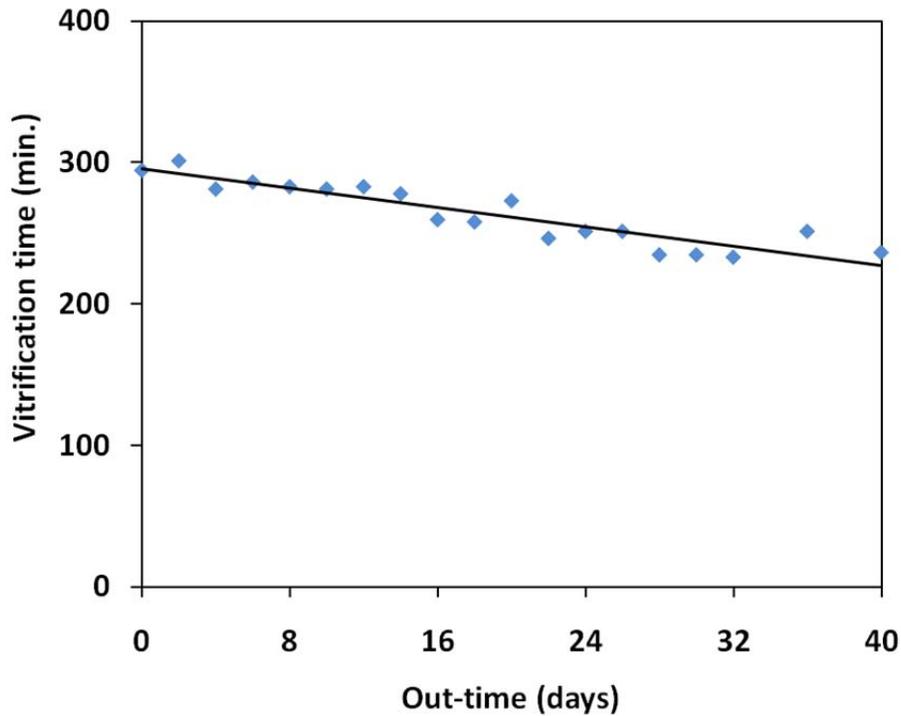


Figure 40. Vitrification time versus out-time (days)

#### 4.2.2 Thermal Analysis

Experimental results from thermal tests for IM7-8552 were represented in this section. To investigate the cure kinetics of autoclave prepreg, thermal parameters including heat of reaction, degree of cure, sub-ambient glass transition temperature and  $T_g$  were obtained for different out-times. Moreover, all the results were plotted against out-time to understand the prepreg behavior and also to track the out-time trend.

#### 4.2.2.1 Heat of Reaction

For the autoclave prepreg the enthalpy of cure was tracked with respect to out-time by integrating the area under the heat flow curve. The calculated enthalpy referred to as heat of reaction was plotted against out-time in Figure 41. A decreasing linear trend was observed for  $H_U$ . This implies that the heat released during the conditioning of samples under the ambient temperature was considerable.

Additionally the residual heat of reaction,  $H_R$  was obtained using a ramp rate of 5.00 °C/min. The experimental result was plotted against out-time in Figure 41. Although an increasing trend was observed for the residual heat obtained from 5320-8HS heat flow curves, no significant changes were observed for the  $H_R$  values for IM7-8552.

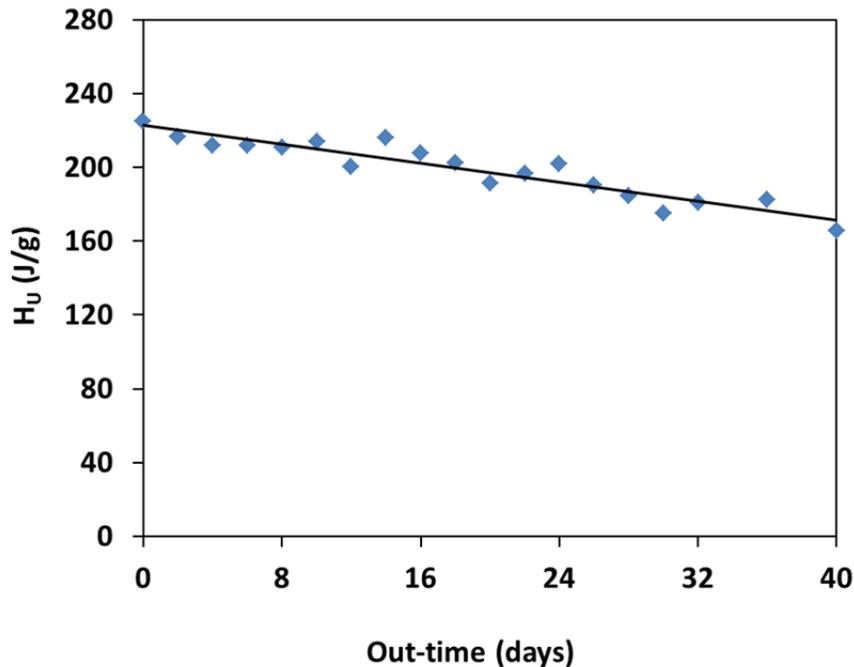


Figure 41. The total heat of reaction for the IM7-8552 autoclave prepreg versus out-times. A linear trend was observed as the prepreg advanced to aging.

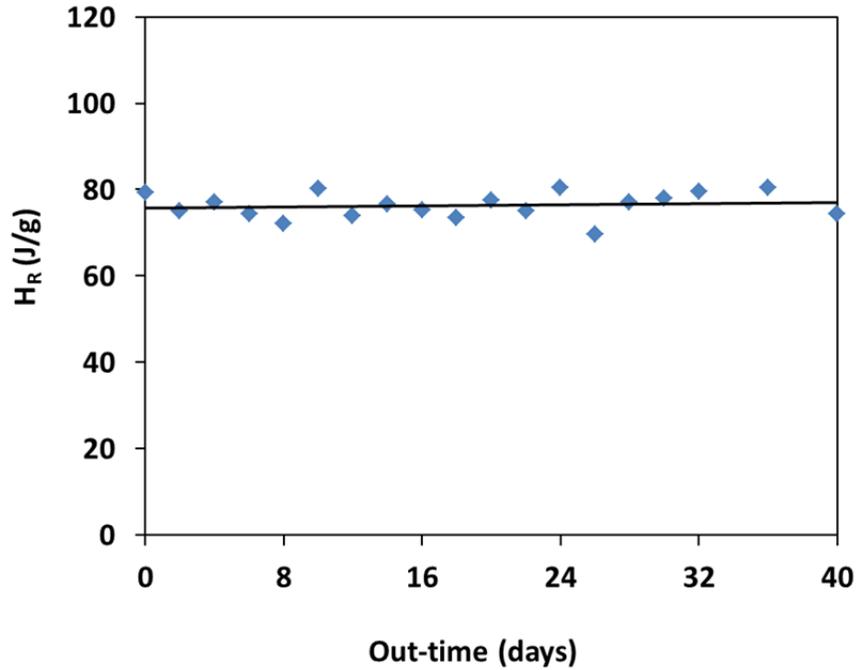


Figure 42. The residual heat of reaction for IM7-8552 that was obtained from the dynamic scan.

#### 4.2.2.2 Degree of Cure

The degree of cure indicates the extent of conversion. In thermal analysis degree of cure measures the progress of reaction based on heat of reaction. In this section, the behavior of  $\alpha$  was described as a function of out-time. Figure 43 represents the changes in degree of cure due to aging,  $\alpha_{Aging}$  with respect to out-time. As shown in this graph, a linear trend was observed for  $\alpha_{Aging}$  as the prepreg advanced to aging. Consequently, the total degree of cure  $\alpha_{total}$  shows a decreasing trend with respect to out-time. This can be explained as a fact that the prepreg sample started to advance in cure during out-time. Thus  $\alpha_{Aging}$  which is the portion of the cure associated with aging advancement was increased.

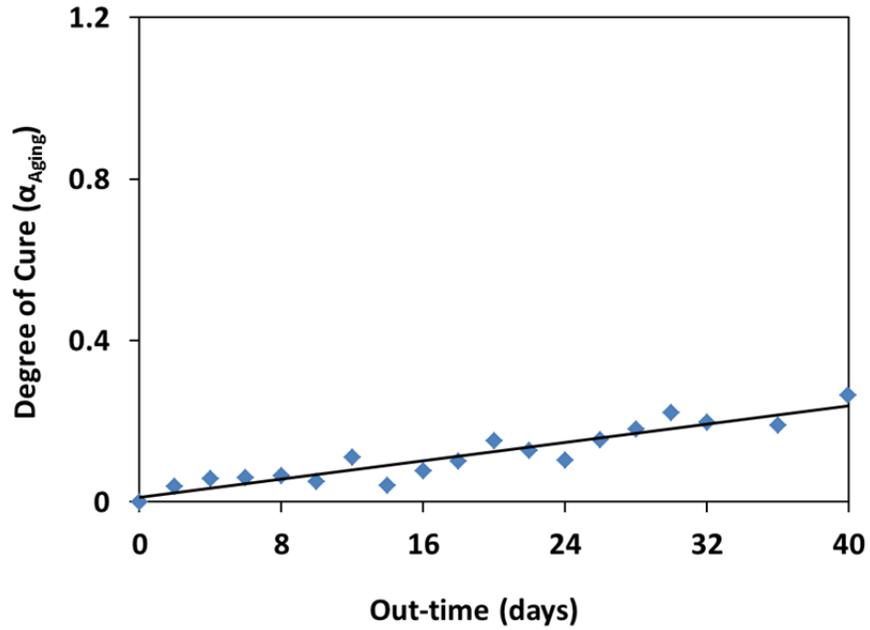


Figure 43. The degree of cure due to aging versus out-times for IM7-8552.  $\alpha_{Aging}$  was increased with a linear trend.

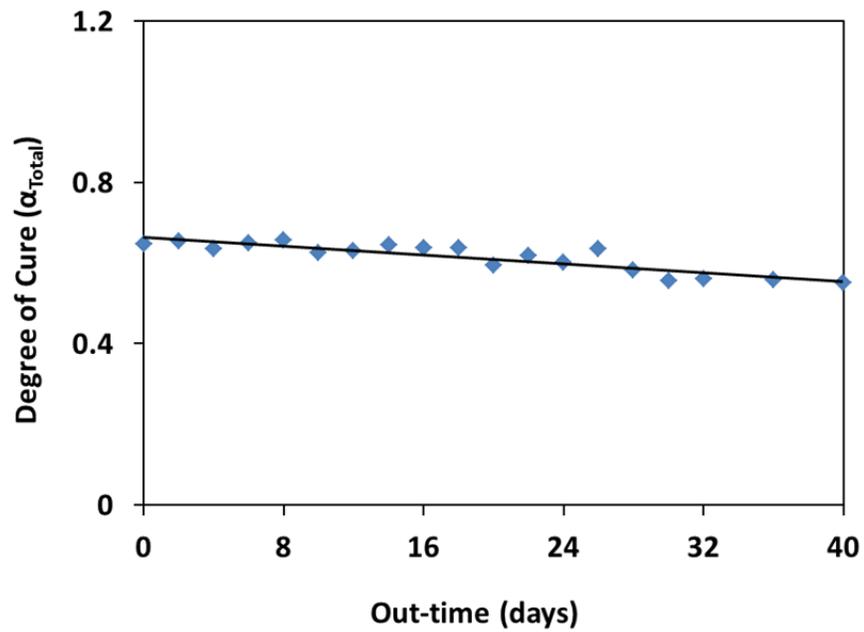


Figure 44. The total degree of cure for IM7-8552 versus out-times. The decreasing trend implies the material advancement in cure under ambient temperature.

#### 4.2.2.3 Sub-Ambient Glass Transition Temperature

As mentioned sub-tg is an important parameter in prepreg processing. In this work, sub-Tg for IM7-8552 out-times up to 40 days was obtained using a DSC dynamic scan. The experimental results were then plotted against out-time in Figure 45. This graph shows an increasing linear trend for sub-tg as the material advanced in aging. This implies that for an unknown out-time, sub-tg could be used to evaluate the advancement of material to aging with an already obtained trend.

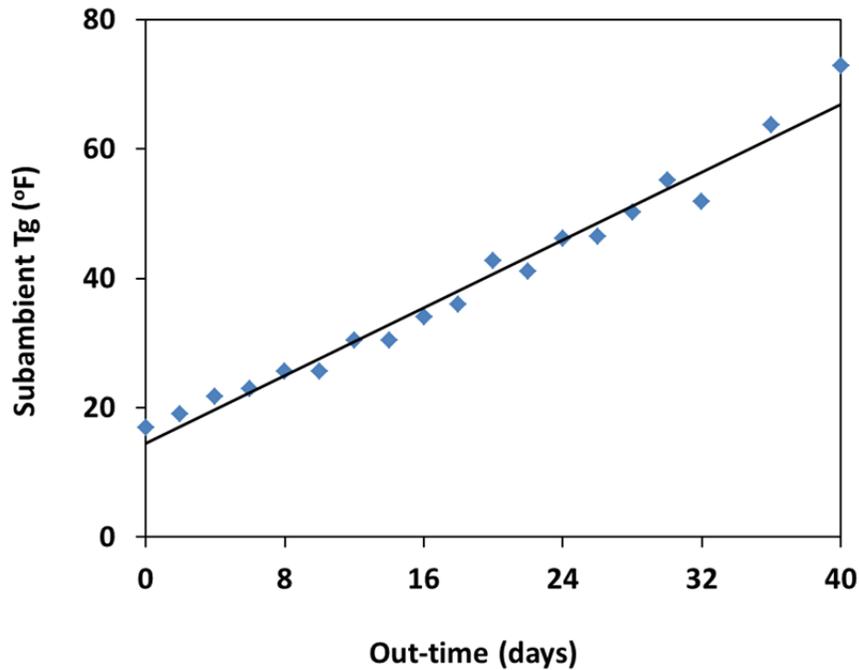


Figure 45. The sub-ambient glass transition temperature versus out-time for IM7-8552. The increasing linear trend represents a new method for evaluating the prepreg out-time.

#### 4.2.2.4 Glass Transition Temperature

Utilizing a 5° C/min ramp rate the glass transition temperature was obtained at the end of each cure cycle for different out-times. The experimental results were then plotted with respect

to the out-time in Figure 46. As shown, Tg was remained almost constant and was independent of the out-time. The stability of glass transition temperature can prove that out-time has minimal effects on the glass transition of prepreg. In this study, all samples were cured using the same cure cycle and thus reached their fully cured state.

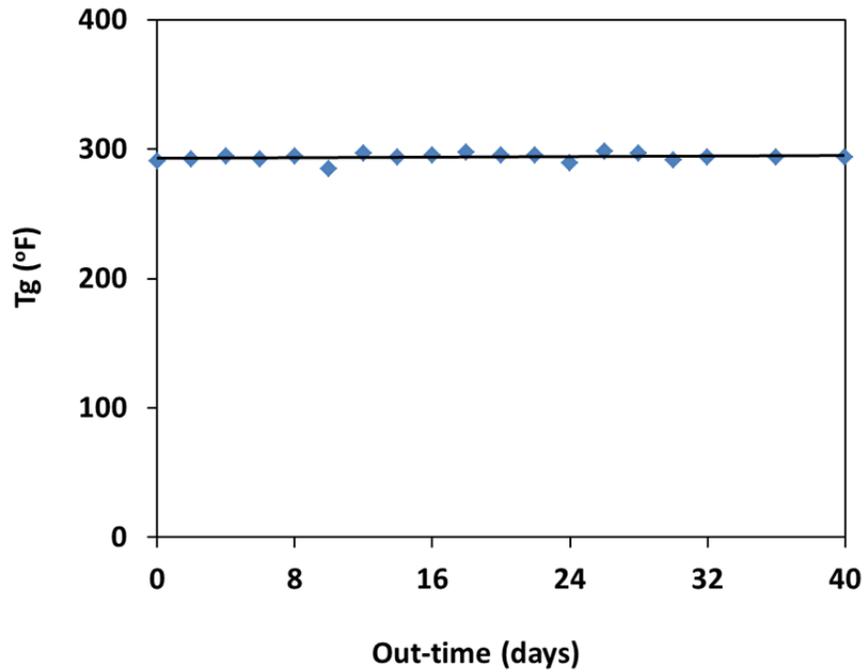


Figure 46. The glass transition temperature Tg versus out-time for IM7-8552 ages samples. The Tg did not show a specific trend and remained constant during out-time study.

## CHAPTER 5

### CONCLUSIONS

#### 5.1 Conclusions

The main purpose of this work was to investigate the prepreg processability and composite properties of 5320-8HS and IM7-8552 prepreg that was aged at ambient temperature for up to 40 days.

Effects of ambient storage on the rheological properties of the prepreg were presented. A strong correlation between out-time, minimum viscosity time, and gel-time was obtained. As such, the real-time monitoring of the prepreg during cure has shown significant changes in viscoelastic properties of aged material compared to pristine material. Although, no change in minimum viscosity time was observed, an increase in minimum complex viscosity and the decrease of gel and vitrification time suggested the problems associated with the processing of the prepreg during cure for the aged material. Furthermore, the linear trend in minimum complex viscosity, gel time, and vitrification time advocate that rheology was a good method in determining the age of prepreg.

Differential scanning calorimetry was utilized to monitor the effects of aging progress on the cure kinetics of an out-of-autoclave and autoclave prepreg. It was observed that the sub-ambient glass transition temperature and percent of conversion due to aging increased proportionally with out-time of prepreg. Total heat of reaction, peak temperature, and activation energy decreased as out-time increased. The correlation between the material out-time and subT<sub>g</sub> of the carbon-epoxy prepreg shows the effectiveness of monitoring material aging using DSC.

## 5.2 Recommendation for Further Studies

The methodology of this work may be further utilized to perform the following:

- To evaluate the effect of premature advancement of cure on mechanical properties of laminated composites. For this purpose, prepreg sheets may be conditioned under ambient temperature and then subsequently cured. Therefore, mechanical properties of aged panels may be compared to the pristine ones.
- The NDT technique could be utilized to examine the quality of aged panels after cure. The experimental results may then be compared to the pristine panels. The C-scan images are indicative of well consolidation as well as the void content of panels.

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