STRESS RELAXATION BEHAVIOR OF CARBON FIBER-EPOXY PREPREG COMPOSITES DURING AND AFTER CURE

A Thesis by

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DEDICATION

To my parents and my sisters
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ABSTRACT

This study presents the experimental results of time-temperature dependent viscoelastic behavior and cure kinetics of two commercial carbon fiber/epoxy prepregs, IM7/977-2 unidirectional tape (UD) and IM7/977-2 plain weave fabric (PW). An in-depth study on the oscillatory and transient rheological behavior of prepreg composites is conducted using a dynamic mechanical analyzer (DMA) and the study of cure kinetics is conducted using a differential scanning calorimeter (DSC). A novel experimental methodology is proposed in this study to describe the stress relaxation behavior of prepreg composites during cure. Time- and cure-dependent stress relaxation behavior of prepreg composites is studied in three in-plane directions: 0, 45, and 90 degrees of the laminates. Several other factors, such as the mismatch of fiber orientation of adjoining plies, stacking sequence of the laminate, and relative position of the plies with respect to the neutral axis are considered to study their effects on the stress relaxation behavior during cure. The stress relaxation behavior of cured composites is obtained by utilizing the time-temperature superposition (TTS) principle. TTS study on UD laminates (in 0, 45, and 90 degree fiber directions) is conducted at four distinct cure states, whereas the PW laminate is studied in the same fiber directions but at a fully cured state only. Experimental results are used to predict the life cycle of the composite products by generating the stress relaxation master curves for different combinations of fiber orientation and cure states.

The study shows that the relaxation modulus during cure is case dependent, which leads to the assumption that the relaxation of process-induced stresses during cure varies for different conditions. Moreover, when comparing the performance of UD and PW prepregs, it shows that the PW laminate relaxes more residual stress than the UD laminate during cure. At cured condition, the PW material shows better long-term mechanical performance than UD material.
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CHAPTER 1
INTRODUCTION

1.1 Motivation

Advanced polymer matrix composites (PMCs) are considered as the ultimate “designer” material [1]. Composite materials are currently used in a wide variety of high-tech industries primarily because of their high specific strength and stiffness as well as its low CTE when compared to traditional structural materials (e.g. steel, aluminum, etc), and so on. However, besides their fascinating aspects, the poor dimensional stability is the major setback to the advancement of composite materials. It has been reported in the literature that the formation of residual stress during processing of PMCs, caused by the heterogeneity of the material [2], is the reason for a loss in dimensional tolerance of the final part via excessive distortion. Residual stress often leads to micro cracking of the matrix system, which compromises the mechanical performance of the structure [3]. Factors that are responsible for the formation of residual stress, some of them are originated from the fundamental nature of the constituents, such as the coefficient of thermal expansion (CTE) mismatch between the resin and fiber, volumetric shrinkage of resin, and so on [1]. Therefore, a complete elimination of residual stress from the composite structure might not be possible at this stage; rather, it can be optimized or taken into account while designing composite structures. In the early stages of the study of residual stress, it was believed that the formation of residual stress was limited to the cooling cycle only, with the laminate resting in a stress-free state prior to cooling [4]. However, more investigation shows that a major portion of the cure cycle contributes to the formation of residual stress [5-13].

Unlike conventional structural materials, polymers show a unique behavior while carrying loads. This behavior is commonly referred to as the “stress relaxation” behavior.
Traditional structural materials have a tendency to hold the stress level for a longer period of time while polymers tend to release the stress as a function of time until it reaches a steady state. Therefore, the stress relaxation behavior during cure determines the ability of the material to release the process-induced stress of the laminate, whereas the relaxation behavior of cured composites determines the time period that they can sustain the load without losing structural integrity. Therefore, the knowledge of stress relaxation behavior of polymer composite materials is vital to the accurate design of large scale composite structures and in predicting the distortion of the structure using the finite element analysis method.

To achieve a better understanding of the stress relaxation behavior of polymers, a significant amount of research is found in the literature. Kim et al [14, 15] have performed some pioneering research on stress relaxation behavior of a variety of thermosetting and thermoplastic matrix composites at different cure stages. They claim that stress relaxation behavior of polymers is strongly dependent on the cure state of the material. In another investigation, Kim et al [16] have proposed that the stress relaxation behavior is ineffective during loading and unloading of the structure if the same loading-unloading rate is used. According to Shrotriya and Sottos [17], the relaxation of fabric laminates depends not only on the relaxation of the matrix system but also the geometry of woven fabric bundles in the warp and fill directions. Masuko and Kawai [18] claim that the tensile stress relaxation behavior of cured composites demonstrates fiber-directional dependency.

However, after doing detailed research on the relevant studies, it is found that the concentration of the previously performed studies either focuses only on the relaxation behavior during cure or on the cured state of the materials. None of these studies have considered a combined study of relaxation behavior of PMCs during cure as well as after cure in order to
understand the behavior of the material from the production line to the end of service life. Few researchers have attempted to study relaxation behavior during cure by conducting experiments at discrete cure states of the material. But, this experimental method is particularly limited by the fact that it doesn’t give a complete understanding of the relaxation behavior of the material as the curing continues. Also, it has been reported in the literature that the geometry of the fiber bundles of the laminate could potentially change the relaxation behavior of the laminate, but there are no such studies found in the literature.

In summary, more investigation is required to understand the specific nature of the stress relaxation phenomenon as well as to overcome the shortcomings of previously performed studies.

1.2 Research Objectives

The overall objective of this thesis is to gain a better understanding of stress relaxation behavior of polymer matrix composites (PMCs) utilizing dynamic mechanical analyzer (DMA) and differential scanning calorimeter (DSC).

The scope of this study will be focused on the stress relaxation behavior of two commercial prepreg systems which have the same resin system but different fiber arrangements. This study will help to identify the effects of fiber arrangements on the stress relaxation behavior of polymer matrix composites (PMCs). Experimental study will be conducted during cure as well as after cure. To obtain an in-depth understanding of the stress relaxation behavior during cure, this study will consider several factors that could potentially affect the relaxation behavior of the laminate such as the stacking sequence, fiber directional mismatch of adjoining plies, and cure state of the material. To study the time-temperature dependent behavior of cured composites, the
experiments will be particularly focused on cure state, fiber orientation, and fiber arrangement of the laminates.
CHAPTER 2
GENERAL BACKGROUND AND LITERATURE REVIEW

2.1 Polymer Matrix Composites (PMCs)

Composite material can be defined as a material that consists of two or more materials combined on a macroscopic scale to form a new material that, if properly designed, exhibits the best qualities of its constituent materials. Unlike metal alloys, the individual materials of composites retain their physical and thermal behaviors. Reinforcing fiber and matrix systems are the two most distinguishable structural components of commonly used advanced polymer matrix composites (PMCs) [19]. Typical reinforcing fibers include carbon, graphite, boron, and aramid, while typical matrices are epoxy, polyamide, and polyester. Reinforcing fibers carry the majority of the load applied to the composite structure, whereas the matrix system helps to achieve a desired shape, transfers the load among fibers, and protects the fibers from adverse environmental conditions.

While traditional monolithic metals and their alloys sometimes have difficulty fulfilling the multifaceted requirements of today’s advanced structural design, advanced PMCs fill these needs well. This is why the arrival of advanced composite materials is considered one of the biggest technical revolutions since the invention of the jet engine in the aerospace industry [19, 20]. Many fascinating features such as their light weight, high specific strength, and modulus, dimensional stability at high temperature, and the ability to tailor the thermomechanical properties for specific applications allow these materials to play the leading role in modern structural engineering. If composite materials are properly designed, they can achieve same strength and stiffness as high-strength steel, yet are 70% lighter [19]. Figure 1 illustrates the
specific strength as a function of specific modulus for conventional materials, composite materials, and virgin reinforcing fibers.

Figure 1 Specific strength as a function of specific modulus for conventional materials, composite materials, and virgin reinforcing fibers [21]

2.2 Processing of PMCs

Depending on the resin type, commonly used PMCs fall into two major categories: thermosetting and thermoplastic. The composite materials used in this study are epoxy-based thermosetting composites; therefore, only the processing of thermosetting composites will be discussed here. Thermosetting polymers are insoluble and infusible after processing because of their three-dimensional and highly interconnected covalent bonds. Commonly used thermosetting polymers include epoxies, polyamides, vinyl esters, phenolics, and so on.

Time, temperature, and pressure are the three most influential processing parameters when manufacturing thermosetting composites. A proper combination of these three parameters
leads to a high quality composite structure. Processing of thermosetting composites can be divided into three different stages: A-stage, B-stage, and C-stage. In the early stage of processing it is called as A-stage material. In A-stage, resin is soluble in certain solvents, soft (liquid like), and has the low molecular weight. To facilitate the processing and handling, composite materials are precured before shipment, commonly known as the B-stage material. At this stage, the material is in a rubbery state, has higher molecular weight, and is less soluble in solvents. When the material undergoes the curing process, it changes from a rubbery state (B-stage) to its final state -- a glassy state (C-stage) with a three dimensional cross-linked network which is insoluble. Figure 2 illustrates the transformation of the material from its initial to final stage.

Figure 2 Structural development of thermosetting composites through polymerization from liquid to hard glassy state [21, 22]
Among the various forms of thermosetting composites, “prepreg” is the type of composite materials that is widely used in the industry to fabricate advanced composite structures. Prepreg is a ready-made tape of composite material with reinforcing fibers impregnated with partially processed resin (B-stage), curing agents, additives, and solvents [22]. Fiber arrangement of prepreg tape could be unidirectional or woven. A prepreg laminate of the desired thickness and fiber orientation is fabricated by laying up sufficient number of prepreg layers in the desired orientation. Conventionally, thermosetting prepreg laminates are processed in the autoclave to obtain a void free, consolidated, and strong laminate. However, continuous research is going on to find ways to cure thermosetting prepregs in ovens to reduce cost and avoid complications that arise due to the rigors of adhering to autoclave processing. Figure 3 shows typical vacuum bagging method for thermosetting composites.

![Figure 3 Schematic of typical vacuum bagging method [23]](image)

It is common practice to cure thermosetting composites using a two-stage cure cycle (see Figure 4). In a two-stage cure cycle, the first dwell permits trapped gasses and excess resins to escape in order to achieve better compaction of the laminate. A judicious choice of time and temperature for the first dwell helps to achieve minimum viscosity of resin while keeping the cure considerably low [12]. On the other hand, the second dwell temperature promotes a three-
dimensional network of the polymers by accelerating the crosslinking reactions. Higher temperature causes higher CTE mismatch between the resin and fiber while lower temperature prolongs the cure cycle. Therefore, these two concerns are considered when choosing the second dwell temperature.

Typically, a constant vacuum pressure is applied to the system until the resin viscosity begins to increase due to excessive crosslinking reactions. As the viscosity begins to increase, the vacuum pressure becomes ineffective in regards to degassing the laminate. Therefore, a constant positive pressure is applied to the laminate to achieve better consolidation and improve the fiber-matrix interaction at the interface [12].

![Temperature and pressure cycle for processing of thermosetting composites](image)

Figure 4 Schematic of a typical temperature and pressure cycle used for processing of thermosetting composites [23]

2.3 Factors Affecting Stress Formation during Processing

2.3.1 Resin Shrinkage

Knowledge of process-induced shrinkage is crucial as it can cause as much as 30% of total process-induced stresses [24, 25]. During the processing of composites, volumetric change of the resin system occurs in multiple stages: (1) thermal expansion of the resin during heating,
(2) chemical shrinkage of the resin due to cross-linking reactions, and (3) thermal contraction of resin during cooling. Second- and third-stage volumetric changes in resin make higher residual stress more likely. During expansion or contraction of the resin system, a deformation gradient is developed at the resin-fiber interface due to the mismatch of CTE between resin and fiber, which induces stress on the interface. Moreover, it has been observed in experimental studies that the total cure shrinkage of a laminate can be significantly different in three principal directions of the laminate. Figure 5(a) demonstrates the profiles for dimension change during cure in three principal directions of UD laminate, while Figure 5(b) shows compressive forces acting on the fibers due to resin shrinkage [26]. Therefore, the variation in cure shrinkage given different directions of laminate creates an even more complicated stress field longitudinally as well as radially [9].

Figure 5 (a) Dimensional change of the laminate in three principal directions of UD laminate during cure (b) cure shrinkage induced stress in three principal directions of fiber

2.3.2 Process Cycle

Constituent components of composite structures exhibit temperature-dependent thermomechanical behavior; therefore, the processing history of composite structures varies with
the cure cycle. High heating/cooling rate and/or cure temperature saves time by accelerating the cross-linking reactions; however, it induces a higher CTE mismatch between resin and fiber which leads to higher residual stress at the end of the cycle. On the other hand, low heating/cooling rate and/or cure temperature induces less residual stress, but involves a longer cure profile. Therefore, it is crucial to keep these opposing phenomena balanced when designing a cure cycle for polymers. An experimental study was performed to investigate the total shrinkages as a function of cure temperatures and heating/cooling rates. Figure 6 illustrates that cure temperatures have a greater effect on total shrinkage than heating and cooling rates. However, it needs to be kept in mind that even though cooling rates do not change the volumetric shrinkage of the laminates, they can still produce significant residual stresses. Madhukar et al. [25] showed that an intelligent cure cycle that follows the changing states of the material, produces less stress during processing than the one with predetermined steps. Figure 7 shows the optimum cure cycle that produced minimum process-induced stress in their study.

![Figure 6 Comparison of total shrinkage for the variation of cure temperature or heating/cooling rate](image)
2.3.3 Stacking Sequence of the Laminate

The tailor-ability of advanced PMCs is widely acknowledged to be one of the biggest advantages of their use. However, despite the beneficial outcomes, it produces higher residual stresses than the laminate that is not tailored such as an UD laminate. Composite plies are considered highly anisotropic with high CTE mismatch between the constituents. Therefore, a laminate having these kinds of plies arranged in different directions possesses not only intra-ply but also inter-ply CTE mismatch, which creates even more residual stress during processing.

From the knowledge of classical lamination theory (CLT), it has been known that the in-plane normal deformation of the laminate may produce bending or twisting moments or in-plane shear stresses depending on the stacking sequence of the laminate. Therefore, the maximum distortion of the laminate shows dependency on stacking sequence of the laminate. Roozbehjavan et al. [27] observed that the lack of symmetry of laminates produces higher distortion than the lack of balance of angle-plies (see Figure 8).
2.3.4 Tool-Part Interaction

Tooling materials used for composite curing are usually isotropic and homogeneous metals while the composite materials are orthotropic and heterogeneous. The magnitude of interaction between the tool and the composite part during cure is dependent on the mismatch of CTE between the tool and the composite part, surface roughness of the tool, rate of relative displacement between tool and part, and the normal pressure applied to the laminate [7]. Coarse surface finish of the tool and autoclave pressure enhances the mechanical interlocking at the tool-part interface, which limits cure-induced expansion and contraction of the laminate. The CTE of common tooling metals are higher than the composites. For instance, the CTE in the fiber direction of a PMCs is around -0.5 μm/m while the tooling materials can have a CTE of up to 24 μm/m (aluminum). The mismatch of CTE between the tool and the composite part induces a gradient of deformation (see Figure 9) at the tool-part interface, and is considered the major contributor of the stresses that develop from tool-part interaction. Figure 10 illustrates the variation of maximum distortion of composite parts for different tooling materials.

Figure 8 Effect of stacking sequences on the distortion [27]
2.3.5 Geometry of the Laminate

Process-induced stress can be affected by the geometry of composite structures, such as the thickness of the laminate, intricacy of the part, the end conditions of the part (i.e., open or closed around the tool), and so on. Thick laminates can suffer greatly from a lack of temperature uniformity through the thickness direction, which creates a gradient of degree of cure. As a result, it develops a spatially varying viscoelastic response that can be a factor in the development of stress in thick laminates [29]. A complex shape can also affect the uniform temperature distribution on the part as well as the interaction between the tool and the part. Closed-end parts like barrel- or mandrel-shaped parts are affected by both lateral and radial expansion and contraction of the tool, which is not common for the open-end parts.
2.4 Theory of Stress Relaxation

Stress relaxation behavior is one of the fundamental natures of polymers. At the time of stress relaxation, polymer molecules rotate and unwind due to the applied strain. The rearrangement of molecules continues as a function of time and reduces stress but maintains the strain level same. Figure 11 schematically illustrates the stress relaxation behavior of three different types of materials: elastic solid, viscous fluid, and viscoelastic material. Purely elastic material holds a constant stress level for an extended period of time; purely viscous material dissipates stress immediately and will come back to zero stress level, while viscoelastic material relaxes stress with time. Relaxation behavior of polymers is more often expressed by the stress relaxation modulus which changes as a function of time.

\[ E(t) = \frac{\sigma(t)}{\varepsilon_0} \]  

where \( E(t) \) is the relaxation modulus, \( \sigma(t) \) is the time-dependent stress, and \( \varepsilon_0 \) is the applied constant strain.

Maxwell developed a mathematical model to describe the characteristic nature of viscoelastic materials by proposing a mechanical analogy between viscoelastic materials and a series combination of spring and dashpot. Here, the spring element represents the elastic nature of the material and the dashpot represents its viscous nature. Figure 12 shows the schematics of

Figure 11 Stress relaxation behavior of three different types of materials subjected to same amount of strain (Courtesy of TA Instruments)
the Maxwell element, where $E$ is the instantaneous tensile modulus of the spring while $\mu$ is the viscosity of liquid in the dashpot. Relaxation time $\tau$ is defined as [30]

$$\tau = \frac{\mu}{E} \quad (2)$$

![Figure 12 Schematics of a Maxwell element](image)

The equation of motion of the Maxwell model [30] can be defined as

$$\frac{d\varepsilon}{dt} = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{\mu} \quad (3)$$

In the stress relaxation experiment, the rate of change of strain becomes zero ($\frac{d\varepsilon}{dt} = 0$) after a constant strain is applied to the system. Therefore, Equation (3) can be written as,

$$\frac{d\sigma}{\sigma} = -dt \frac{E}{\mu} = -\frac{dt}{\tau} \quad (4)$$

Integration from $\sigma_o$ at time 0 to $\sigma(t)$ at time $t$ gives

$$ln\sigma(t) = ln\sigma_o - \frac{t}{\tau} \quad (5)$$

The exponential is then dividing by $\varepsilon_o$ on both sides

$$\frac{\sigma(t)}{\varepsilon_o} = \frac{\sigma_o}{\varepsilon_o} e^{-\frac{t}{\tau}} \quad (6)$$

which simplifies to

$$E(t) = E e^{-\frac{t}{\tau}} \quad (7)$$

where $E$ is the modulus of the spring, $E(t)$ is the tensile stress relaxation modulus, $t$ is the time, and $\tau$ is the relaxation time.
2.5 Literature Review

Kim and White [15] were the first to perform a systematic investigation on the stress relaxation modulus and relaxation spectrum of polymers. It was suggested from the study that, after gelation, stress relaxation behavior of polymers become extremely dependent on the cure state of the material. They utilized a simplified Prony (exponential) series to describe the time-dependent viscoelastic nature of neat 3501-6 epoxy resin.

\[
E(\alpha, \xi) = E^\infty + (E^u - E^\infty) \sum_{\omega=1}^{N} W_\omega \exp\left[\frac{-\xi(\alpha, T)}{\tau_\omega(\alpha)}\right]
\]

where \(E^\infty\) is the fully relaxed modulus, \(E^u\) is the relaxation modulus in unrelaxed state, \(W_\omega\) are weight factors, \(\tau_\omega\) are discrete relaxation times, and \(\xi\) is the reduced time. Figure 13 shows an excellent fit of the model to the experimental data.

Figure 13 Master curves of stress relaxation behavior of 3501-6 resin at different cure states [15]
Using the findings of previous work [15], Kim and White [14] continued to investigate the stress relaxation behavior of AS4-3501-6 composite material during cooling from cure temperature (177 °C) to room temperature (25 °C) with a cooling rate of 2.5 °C/min. The study showed that the process induced stress at the free edge of the laminate can decrease as much as 30% of its initial magnitude due to stress relaxation.

The study of Kim and White [14, 15] was limited to the gelled state of the material only. To overcome the limitation of their study, O’Brien et al. [31] performed a similar type of study for the entire range of cure state of EPON 862, a di-functional epoxide. Pregelation characterization was performed by using parallel plate rheometry while characterization at post-gelled state of the material was conducted using three-point bending method in the DMA. Eventually, the mechanical properties from the DMA were converted to shear rheometry data to make it experimental method independent. Figure 14 shows the shear stress relaxation master curve for the entire range of the cure.

![Shear stress relaxation master curves of EPON 862over the entire range of cure](image)

Figure 14 Shear stress relaxation master curves of EPON 862 over the entire range of cure (i.e., $0 \leq \alpha \leq 1$)

Zarrelli et al. [32, 33] conducted a series of experimental and analytical studies to formulate a constitutive model to predict the evolution of resin viscoelastic modulus during cure.
The constitutive model was developed based on the assumption that the mechanism underlying the evolution of glass transition temperature and the relaxation time shift during cure is the same. The normalized potential function of $T_g$ and relaxation time ($\tau$) showed a very good agreement with this assumption (see Figure 15). By introducing these potential functions to predict structural evolution, a modified Kohlrausch-Williams-Watts (KWW) model was implemented to determine the relaxation behavior of polymers during cure. The general form of the model was obtained:

$$E(t, T, \alpha) = E_{\infty}(\alpha). e^{-\left(\frac{\xi(T,\alpha)}{\tau_p(\alpha)}\right)^{\beta(\alpha)}}$$

where $\beta$ and $\tau_p$ are material characteristic dependent constants, $E_{\infty}$ is the fully relaxed modulus of the material, and $\xi$ is the reduced time.

![Figure 15](image.png)  

Figure 15 Normalized glass transition temperature and relaxation time potential functions as a function of cure state of the material alongside the Di Benedetto model [32]
However, to achieve a complete understanding of the behavior, it requires knowledge at macro scale as well as in the micro scale. Abadi [34] employed both analytical and finite element analysis to describe the stress relaxation behavior of graphite/epoxy composite on a microscopic scale by considering a representative unit cell of resin and fiber. It was found from the analysis that transverse and longitudinal shear stress were fiber volume fraction dependent at the initial stage of the time domain. Zhou et al. [35] conducted another micromechanical study of the time-dependent deformation of individual fibers of graphite/epoxy composites at elevated temperatures and compared with the analytical formulation.

Masuko and Kawai [18] studied the relaxation behavior of cured unidirectional carbon/epoxy composites as a function of strain rates and fiber direction. Experiments were performed at an elevated temperature (100 °C) by applying different strain rates. It was concluded that high strain rate can significantly affect the stress relaxation behavior of angle-ply laminates.

 Typically, resin is considered as the primary source of the viscoelastic nature of laminates. However, Oskouei and Taleie [36] suggested that in addition to the resin, reinforcing fibers of the laminate could be a factor in the relaxation of the laminate. They studied the effect of different types of fiber materials as well as various arrangements of fibers. Carbon fiber showed the least amount of relaxation while aramid showed the maximum. Stress relaxation experiments were performed for an extended period of time (1000 hr) on carbon fiber-, glass fiber-, and aramid fiber-composites under constant loading and in a controlled environmental condition. Higgenbotham-Bertolucci et al.[37] performed an interesting investigation on creep and stress relaxation behavior for three different styrene polymers. The effective temperature range of the TTS experiment was extended from room temperature to well above the \( T_g \) of the
corresponding material. Analysis of shift factors of the master curves indicated that at relatively high temperatures shift factors followed the WLF model while at lower temperatures a linear model described them better. The transition temperature of these two models and the glass transition temperature were so close that this transition could be represented as the $T_g$ of the material.

Figure 16 Proposed model for shift factors of stress relaxation and creep experiments.

Lee-Sullivan [38] studied the effect of cooling rates on the stress relaxation of polyvinylidene fluoride (PVDF). The microstructure of semicrystalline polymer is dependent on the process history of the material which ultimately governs the mechanical behavior of the polymer on a macro scale. In the Lee-Sullivan’s study, specimens were cooled from 60 °C (the upper service temperature) to room temperature with different ramp rates to achieve distinct microstructures, and then stress relaxation experiments were performed. They concluded that the microstructure can potentially change the stress relaxation behavior of composites.

Kim and Sun [16] proposed a single-parameter model to predict the stress-relaxation and stress-recovery behavior of AS4/PEEK thermoplastic composite material during loading and unloading. It was proposed from the analysis that equilibrium stress-strain curves during loading
and unloading are quite similar in nature, and both situations can be described by the proposed model,

\[
\bar{\sigma} = a(1 - b\dot{\varepsilon}^m)(t)^n
\]  

where \(a = 0.969\), \(b = 0.093\), \(m = -2.09\), \(n = 0.21\), and \(\dot{\varepsilon} = \text{strain rate}\).

It has been reported in the literature that creep and stress relaxation behaviors originate from the same physical phenomenon of viscoelastic material but are expressed differently [39]. Gates et al. [40] performed a combined experimental and analytical investigation on the creep compliance of IM7/K3B composite as a function of physical aging time and temperature. Experiments were conducted to obtain the compliances in two resin dominated directions, shear and transverse directions, in tension and compression modes. Their investigation showed that, regardless of aging time and temperature, compression loading induces higher compliance than tension loading.

A semi-phenomenological approach was reported by Baeurle et al. [41] in order to predict the stress relaxation behavior of inhomogeneously crosslinked thermoplastic elastomers for an extended period of time. Typically, the fluctuation of DOCs is caused by thermal fluctuation during processing. The relaxation of inhomogeneously crosslinked polymers for large time \(t \gg \tau_o(T)\) was expressed by the following equation:

\[
E(t, T) \approx E_{t \to \infty}(T) \times \left[1 + \frac{C_1}{\langle n \rangle} \frac{t}{\bar{\tau}^*(T)} \left(\frac{1}{\gamma + \delta}\right) \exp \left(-\left(\frac{t}{\tau^*(T)}\right)^{\frac{1}{1 + \delta}}\right)\right] \tag{11}
\]

where \(\delta\) and \(\sigma\) are parameters dependent on the type of network motion under consideration, \(\tau^*\) is the characteristic relaxation time, \(C_1\) is a constant, \(T\) is the temperature, \(\langle n \rangle\) is the average domain size, and \(\gamma\) is the power law exponent.
2.6 Limitations

The literature review presented in the previous section indicates that a great deal of experimental and analytical studies have already been performed with the aim of achieving a better understanding of the time- and temperature-dependent viscoelastic nature of polymers. These studies include the stress relaxation (SR) behavior of polymers during and after cure, factors affecting the SR behavior, phenomenological behavior in the macro and microscopic level, and so on. All these studies have made the SR behavior of polymers more comprehensible. However, they still fall short of describing some fundamental SR behaviors of PMCs, such as the true SR behavior of PMCs during cure and the correlation between the SR modulus and the mechanical modulus. None of these works has reported any detailed study on the sources of the variation of SR behavior for different materials or the factors that potentially affect SR behavior during cure. Studies conducted to describe the SR behavior of polymers during cure were limited to some discrete cure states of the material; moreover, it is believed that the experimental approach used may not be the best way to describe this phenomenon. The commonly observed approach to find the SR behavior of PMCs is done by combining the viscoelastic behavior of resin and the elastic properties of fibers, which may not necessarily represent the real composite materials all the time. In most cases, the interaction between resin and fibers at the interface is ignored.

The vast majority of the studies performed for cured composite materials are focused on the single type of material only even though it is explicitly mentioned in the literature that the fiber type or the arrangement of fibers of the laminates could affect the relaxation behavior of the laminate [36]. All the experiments of cured composites focus on determining the time-
temperature dependent viscoelastic behavior of composites rather than illustrating the time-
temperature dependent behavior of composite materials for their entire life cycle.
3.1 Materials

Two commercial prepregs, IM7/977-2 unidirectional tape (UD) and IM7/977-2 plain weave fabric (PW) (see Figure 17) were used in this study. These two epoxy based prepregs are manufactured by Cytec and are widely used in the aerospace industry due to their superior performance. Both prepreg systems have HexTow™ IM7- are continuous, high strength, moderate modulus, and Polyacrylonitrile (PAN) based carbon fibers [42], which are impregnated with 977-2 toughened epoxy resin manufactured by CYCOM®. Since the true composition of the resin systems is unknown due to the proprietary obligation of the manufacturer, it is assumed that the fiber arrangement is the only difference between these two prepregs. For the sake of brevity, IM7/977-2 tape and IM7/977-2 fabric will be referred as the UD and PW materials, respectively, for the rest of the study.

CYCOM® 977-2 is a 177 ºC curing resin which is recommended to process in the autoclave. Typically, it comes with a shelf life of 12 months at -18 ºC and 42 day at 22 ºC. This extended out-life makes it suitable for the fabrication of large-scale composite structures [43]. Both prepreg systems are especially designed for high performance primary or secondary structures of aircraft, space structures, cryogenic tanks, and other advanced applications where light weight and impact resistance is of primary issue. Table 1 shows the manufacturer’s recommended cure cycle (MRCC) for this resin system.
TABLE 1
MRCC FOR IM7/977-2 UD AND IM7/977-2 PW MATERIALS

<table>
<thead>
<tr>
<th>Cure Procedure</th>
<th>UD/PW Prepreg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ramp rate</td>
<td>0.6 - 2.8 °C/min</td>
</tr>
<tr>
<td>Cure temperature</td>
<td>177 °C</td>
</tr>
<tr>
<td>Cure time</td>
<td>3 hours</td>
</tr>
</tbody>
</table>

Figure 17 Schematics of (a) unidirectional (UD) prepreg and (b) plain weave (PW) prepreg

3.2 Study of Cure Kinetics

3.2.1 Differential Scanning Calorimeter (DSC)

Q2000 DSC from TA Instruments (New Castle, DE) was used to study the cure kinetics of prepreg composites during processing. Differential scanning calorimeter (DSC) measures the quantitative difference of temperature and heat flow as a function of time and temperature between the target and reference materials when heat evolves from the chemical reaction within the target material [ASTM E473]. There are two different types of DSCs available: power compensating and heat flux. A power compensating DSC has two separate heaters for the reference and sample materials, and the temperature difference between them is compensated by
supplying differential power to the heaters. On the other hand, a heat flux DSC has a single heater for both reference and sample and the temperature difference between them is measured by highly sensitive and precise thermocouples.

Both methods have their advantages and disadvantages. By incorporating the best features of both technologies, TA Instruments has introduced a new technology in the Q2000 DSC, commonly referred as Tzero technology. In addition to the sample and reference thermocouples, Tzero technology uses one additional central thermocouple to measure the heat flow ($T_0$ thermocouple). Figure 18 shows a typical sample/reference platform and assembly of sensors of the Tzero technology. In addition to the temperature difference between sample and reference, this new method also measures the temperature difference between the sample and the $T_0$ sensor [44].

![Figure 18 A typical sample/reference platform and sensor assembly of Q2000 DSC [44]](image)

### 3.2.2 DSC Sample Preparation and Experimental Method

To study the cure kinetics of UD prepregs, specimens with an approximate weight of 11.5 mg were prepared, encapsulated in the Tzero aluminum pan, and then studied using the DSC.
In order to obtain the time-dependent degree of cure (DOC) profile for the proposed cure cycle, the ultimate heat of reaction \((H_U)\) at \(T_{\text{cure}}\) temperature must be known. Isothermal and dynamic DSC scans are two widely used methods to obtain the \((H_U)\) of polymers [45-48]. Figure 19 shows the schematic of the thermal cycle used in this study to obtain the DOC during cure.

The specimen was equilibrated at 25 °C for 10 minutes, and then it was heated from 25 °C to the cure temperature \((T_{\text{cure}}=177 \, \text{°C})\) with a heating rate of 2.78 °C/min. The specimen was cured at that temperature for 500 minutes, and the heat flows to or from the specimen was recorded continually. The total heat of reaction \((H_T)\) was calculated by adding the heat of reaction for the heating stage to that of the isothermal. After the completion of the isothermal scan, the specimen was cooled down from 177 °C to 25 °C with a very high cooling rate (≈ 100 °C/min) to avoid any dissipation of heat during cooling [49]. Following the rapid cooling, two consecutive dynamic scans were performed by heating the specimen from 25 °C to 290 °C with a heating rate of 3 °C/min. The temperature during the dynamic scan reached beyond the \(T_g\) of the sample material, and it resumed the chemical reactions again and led to the state of complete chemical conversion of the material. Heat of reaction extracted from the dynamic scan was designated as the residual heat of reaction \((H_R)\). A second dynamic scan was performed to ensure that there was no heat of reaction left after the first scan. The ultimate heat of reaction \((H_U)\) was achieved from the summation of \(H_T\) and \(H_R\).

\[
H_U = H_T + H_R
\]  
(12)

Degree of cure (DOC) of the specimen was determined from the ratio of total heat of reaction at time \(t\) \((H(t))\) to the ultimate heat of reaction \((H_U)\)

\[
\alpha(t) = \frac{H(t)}{H_U}
\]  
(13)
To correlate the experimental results with the analytical study, several models were reported in the literature. Among those, Barrett [50], Kamal [1], and Springer-Loos [45] were found to be the most recognized cure kinetics models. In this study, however, only the Springer-Loos model was utilized to investigate how well this model fits with experimental data. This model was defined as

\[ \frac{d\alpha}{dt} = (k_1 + k_2\alpha)(1 - \alpha)(B_1 - \alpha) \]  \hspace{1cm} (14)

\[ K_i = A_i e^{-\frac{\Delta E_i}{RT}} \]  \hspace{1cm} (15)

where \( B_1 \) is a constant, \( K_1 \) and \( K_2 \) are rate constants dependent on the universal gas constant (R), absolute temperature (T), activation energy (\( \Delta E_i \)), pre-exponential factors (\( A_i \)), and \( \frac{d\alpha}{dt} \) is the rate of change of DOC.
3.3 Study of Rheology

3.3.1 Dynamic Mechanical Analyzer (DMA)

Dynamic Mechanical Analysis (DMA) is viewed as one of the most versatile and reliable experimental techniques available. It has been used for decades to study the rheology of many kinds of polymers and polymer matrix composites. Its precision in identifying mechanical transitions of polymers makes it the most favorable material characterization technique for this study.

![Critical components of a Q800 DMA][51]

Q800 DMA from TA Instruments (Newcastle, DE) was used to investigate the rheological behaviors of PMCs. Q800 DMA has some exclusive capabilities that help it to perform with high precision. For instance, it uses a non-contact, direct drive motor which is built from high performance composites, ensures the low compliance of the system. The drive shaft is supported by a thin layer of air which allows it to float without any mechanical contact.
Additionally, it uses a highly specialized optical encoder to measure displacement that enables it to achieve a resolution of 1nm [52].

In order to facilitate the study of different rheological phenomena of PMCs at distinctive loading conditions, the Q800 DMA has two major types of clamping fixtures: tensioning (3-point bend, film-tension, fiber-tension, compression, and penetration clamps) and non-tensioning (single/dual cantilever, shear sandwich, and submersion clamps). In this study, the film-tension clamp was used extensively to characterize diverse rheological phenomena of thermosetting composites. In the tension mode, the load applied to the specimens can be either transient (static) or oscillatory (dynamic).

The quality of prepared samples is always a factor to the accuracy and reliability of the experimental results. Since there are not enough standardized procedures available for the DMA viscoelastic analysis, the recommendation from TA Instruments is followed consistently throughout the study. TA Instruments confines the proportionality between mechanical strength and geometry of the samples into a provided envelope. Figure 21 illustrates that the combination of mechanical modulus and geometry factor (GF) must always stay inside the envelope while using the tension clamp. The geometry factor (GF) of the specimens is typically defined by the following relation

\[ GF = \frac{L}{A} \]  

where \( L \) is the length of the specimen (mm) and \( A \) is the cross sectional area (mm\(^2\)) of the specimen.
Figure 21 Recommended range of geometry factor (GF) for the fiber-tension clamp samples [51]

Figure 22 Typical size of the prepreg samples used in this study and mounting method of the samples on the DMA film-tension clamp

### 3.3.2 Oscillatory Rheology

Mechanical behavior of polymers falls between pure elastic and pure viscous materials and commonly referred as “viscoelastic” behavior. By applying dynamic loading, the dynamic mechanical analyzer (DMA) can characterize various viscoelastic properties. According to the basic working principle of dynamic mechanical analysis (DMA), an oscillating (sinusoidal)
stress or strain is applied to the specimen, and the response of the specimen is measured in terms of magnitude of deformation of the specimen and the phase leg (δ) between the input and response signals. These are the key information to determine the state of the material (i.e., modulus, viscosity, transition state of the material, etc.) [53]. Figure 23 illustrates how the viscoelastic materials respond when sinusoidal stress is the input signal.

![Figure 23 Response of viscoelastic material corresponding to the sinusoidal stress or strain [53]](image)

\[ \varepsilon(t) = \varepsilon_0 \sin \omega t \]  \hspace{1cm} (17)

\[ \sigma(t) = E \cdot \varepsilon(t) = E\varepsilon_0 \sin \omega t = \sigma_0 \sin \omega t \]  \hspace{1cm} (18)

In this equation \( \sigma(t) \) is the stress at time \( t \), \( \sigma_0 \) is the applied maximum stress, \( \omega \) is the frequency of oscillating stress, and \( t \) is the time. Pure elastic materials respond instantly with the applied stress showing no phase lag (\( \delta=0^o \)) between the input signal and response signal. Shear stress on the viscous liquid is proportional to the strain rate. Therefore, the applied oscillating strain can be expressed as

\[ \gamma(t) = \gamma_0 \sin \omega t \]  \hspace{1cm} (19)

\[ \tau(t) = \eta \cdot \dot{\gamma}(t) = \eta \cdot \frac{d\gamma(t)}{dt} = \eta \cdot \omega \gamma_0 \cos \omega t = \eta \omega \gamma_0 \sin(\omega t + \frac{\pi}{2}) \]  \hspace{1cm} (20)
This shows that the resultant stress on a viscous liquid is 90 degrees out of phase ($\delta = 90^\circ$) of input strain. Since viscoelastic materials fall between pure elastic and pure viscous materials, the stress due to the strain described in equation (18) can be written as

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) \quad 0^\circ \leq \delta \leq 90^\circ$$

(21)

### 3.3.2.1 Mechanical Modulus and Viscosity during Cure

PMCs undergo a vigorous change of state of the material when transforming from a rubbery to glassy state during processing. During this period, the mechanical modulus of the polymer is usually reported by a quantity commonly referred as the complex modulus ($E^*$), which is derived from the complex variable treatment of the sinusoidal deformation of the specimens [44]. The complex modulus ($E^*$) can be expressed as:

$$E^* = \frac{\sigma(t)}{\varepsilon(t)} = \frac{\sigma_0}{\varepsilon_0} e^{i\delta} = \frac{\sigma_0}{\varepsilon_0} (\cos \delta + i \sin \delta) = E' + iE''$$

(22)

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos \delta$$

$$E'' = \frac{\sigma_0}{\varepsilon_0} \sin \delta$$

where $E'$ (real part) of the complex modulus is the storage modulus, which determines the ability of the material to respond elastically and $E''$ (imaginary part) is the loss modulus, which determines the material’s ability to absorb energy through viscous deformation. Tan Delta ($\tan \delta$) is defined as the ratio of $E''$ to $E'$ (during each oscillating deformation cycle).

$$\tan \delta = \frac{E''}{E'}$$

(23)

Based on the deformation amplitude and the phase lag of the deformation cycles, the viscosity of the polymer can be determined as well. Viscosity changes significantly throughout the curing process, and that is why the viscosity is frequently used to indicate the state of the
material. Similar to the complex modulus ($E^*$), complex viscosity ($\eta^*$) has its real and imaginary components of viscosity, where the real component represents the viscous nature and the imaginary component represents the elastic nature. It is defined as

$$\eta^* = \frac{E^*}{2(1 + \nu)}$$ (24)

$$\eta^* = \eta' - i\eta''$$ (25)

where

$$\eta' = \frac{\tau_o}{\omega \gamma_o} \sin \delta$$ (26)

$$\eta'' = \frac{\tau_o}{\omega \gamma_o} \cos \delta$$ (27)

Specimens (22mm×2mm×0.25mm) were prepared from uncured laminates of both UD and PW prepregs. Prepared specimens were mounted on the film-tension clamp and cured in the DMA furnace using the recommended cure cycle. An oscillating strain of 0.01% and frequency of 1Hz was applied to the specimens to obtain various viscoelastic properties of the subjected specimen during cure. A continuous flow of inert purging gas (99.99% pure N₂ gas) was maintained around the specimens while curing. It was assumed that the effect of pressure would be too small for the size of the specimen used in DMA analysis. The data collection was continued only until the end of the isothermal cure stage due to the amount of noise picked up by the DMA during cooling. It was assumed that the viscoelastic properties did not change significantly during cool down.
3.3.2.2 Determination of Linear Viscoelastic Region (LVR)

Within the LVR, DMA collects the response of the materials without destroying their structure [54]. Therefore, the specific limit of linear viscoelasticity was needed for experiments where the transient (i.e., static) loading condition would be applied. Most frequently this limit of linear viscoelastic region (LVR) is expressed by a range of strain or deformation-amplitude.

Linear viscoelastic regions of the specimens were determined from the strain-sweep experiments in the DMA. Deformation amplitude (or strain) of the specimens was increased incrementally from 1µm to 50 µm with a fixed frequency of 1 Hz, and the change of storage modulus during this period was recorded. Normalized storage modulus was plotted against the strain or amplitude to achieve the LVR in terms of each, respectively. The end limit of LVR could be identified from the plot by choosing the strain or amplitude from the horizontal axis, which corresponds to the 5% change of storage modulus as compared to the initial magnitude.
3.3.2.3 Determination of Glass Transition Temperature ($T_g$)

The glass transition temperature ($T_g$) of the polymer is defined by the temperature beyond which the translational motion of polymer chains becomes active and, as a result, the material changes from a glassy to rubbery structure. Typically, the $T_g$ of thermosetting polymers is identified in the DMA by a sudden reduction in mechanical performance of polymers by several orders of magnitude or by the peak of tan δ or loss modulus as presented in Figure 26. Specimens of approximate size of 22.5mm×1.5mm×0.2mm were prepared, and the experiments were conducted in the DMA in strain controlled mode by applying an oscillating strain of 0.02%. After equilibrating the specimens at 30 °C for 10 minutes, the temperature was increased from 30 °C to 220 °C with a heating rate of 5°C/min. Figure 26 illustrates the typical ways to find the $T_g$
of PMCs. Even though the peak of tan δ is frequently cited as $T_g$ in the literature, here the peak of loss modulus is reported as the $T_g$ suggested by the standard ASTM E1640-07.

![Figure 26. Typical approaches to find out the Tg of PMCs using DMA](image)

### 3.3.3 Transient Rheology

In transient rheology, rheological behaviors were obtained by applying transient or constant loading (i.e., stress or strain) to the specimens. Transient rheology of the selected PMCs was studied during cure as well as partially or fully cured specimens. Depending on the type of the experiment, the magnitude of loading varied.

#### 3.3.3.1 Total Cure Shrinkage (TCS)

To have a better understanding of the relation between the stress formation and total cure shrinkage (TCS) of UD laminates, a brief experimental study was performed on TCS in three principal directions of laminates as well as the effects of process cycles on the TCS. Rectangular samples (2- to 6-ply thick) were prepared to obtain the TCS in longitudinal and transverse directions while cylindrical (24-ply thick) samples were prepared for through-thickness
direction. The laminates were debulked for half an hour at 25-27 in Hg vacuum pressure before preparing the samples. Study of TCS was performed in three principal directions of UD laminates for the recommended cure cycle (MRCC) as well as the customized cure cycles.

3.3.3.2 Stress Relaxation during Cure

Specimens of 22mm×4mm were fabricated from prepreg laminates of different thicknesses (2-4 plies) to investigate the stress relaxation (SR) behavior during cure. SR during cure of UD laminates was studied as a function of both time and DOC to illustrate the characteristic behavior from both points of views. In addition to the study of SR of UD laminates in the single fiber direction during cure, other factors that were considered included fiber orientation mismatch, stacking sequence, relative position of plies in the z-direction, and SR behavior at different time periods of the dwell stage. Sufficient care was taken to keep the specimen sizes as close as possible to avoid the inclusion of errors due to the sample size variation. The specimens from PW prepreg were fabricated by following the same procedure, to compare the performance between UD and PW prepregs.

Before mounting the specimens in the DMA, the gripping sections of the specimens were wrapped with thin aluminum foil so that excess resin from the specimens could not contaminate the clamp. A strain of 0.01% was chosen to keep the deformation of the samples as low as possible. Table 2 lists the types of samples fabricated from UD and PW laminates and the purpose of each sample type. It is worth mentioning that the axis of loading was always considered as the axis of reference for all fiber directions.
### TABLE 2
LIST OF STACKING SEQUENCES AND THE PURPOSE OF THE STUDIES

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Sample Type</th>
<th>Stacking Sequence</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>UD</td>
<td>1</td>
<td>[0/0], [0/15], [0/30], [0/45], [0/60], [0/75], [0/90]</td>
<td>Study the effect of angular mismatch between adjacent plies</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>[0/45/90], [90/0/90], [45/0/-45], [90/90/90]</td>
<td>Study the effect of stacking sequence</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>[0/90/-45/45], [0/-45/45/90], [0/45/90/-45], [45/0/-45/90]</td>
<td>Study the effect of relative position of plies</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>[0/0/0/0], [45/45/45/45], [90/90/90/90]</td>
<td>SR behavior of UD laminates in different fiber directions.</td>
</tr>
<tr>
<td>PW</td>
<td>1</td>
<td>[0/0], [45/45]</td>
<td>SR behavior of PW laminates in different fiber directions.</td>
</tr>
</tbody>
</table>

3.3.3.3 **Stress Relaxation of Cured Laminate: Time-Temperature Superposition (TTS)**

When polymers are loaded, they undergo a molecular rearrangement as a function of time that helps to reduce the load by compensating localized stress [55]. The time-dependent short-term behavior of polymers can be characterized easily using currently available technologies, but the long term behavior, which may take few hours to few decades, is nearly impossible to study using the same approach.

However, Tobolsky and Andrew [56] proposed that a similarity exists between time- and temperature-dependent mechanical behavior of polymers, which is now commonly known as the
time-temperature superposition (TTS) principle. According to the TTS principle, mechanical behavior of polymers at high temperature is equivalent to the behavior of the material in longer time intervals (i.e., low frequency), and vice versa. Therefore, the short-term behavior of the material at different temperatures can be utilized to calculate the long-term behavior at a certain temperature. Figure 27 demonstrates how the individual tensile stress relaxation curves at different temperatures can be used to form a composite curve, known as the “master curve”, to extrapolate the mechanical behavior for longer time periods.

![Figure 27 Construction of the master curve from five distinct curves](image)

Figure 27 Construction of the master curve from five distinct curves [30]

One curve is chosen as a reference, and a linear shift is performed along the horizontal axis (typically representing time or frequency) with respect to the reference curve to form a smooth master curve. The amount of horizontal shifting required before superimposing is expressed by the horizontal shifting factor \( a_T \). Here, the subscript \( T \) indicates that the shift factor is temperature dependent. There are two widely known methods to obtain horizontal shift factors. The first one is the Williams-Landel-Ferry (WLF) equation [57],
where $T_o$ is the reference temperature (in K), $T$ is the temperature of interest (in K), and the constants $C_1=17.44$ and $C_2=51.6$ if $T_g$ is used as the reference temperature $T_o$. Typically, the WLF equation is used to characterize the time-temperature-dependent behaviors of polymers above the glass transition temperature [55, 58].

Another common method to find out the $a_T$ as a function of the temperature is based on the Arrhenius equation,

$$\log a_T = -\frac{E_a}{2.303R} \left( \frac{1}{T} - \frac{1}{T_g} \right)$$  \hspace{1cm} (29)$$

where $E_a$ is activation energy related to relaxation and $R$ is the universal gas constant (8.314 J/mole °C). The Arrhenius equation is mainly used to describe the $\beta$- and $\gamma$-relaxation of the polymers otherwise referred to as the relaxation below $T_g$ [58]. The Arrhenius equation is used extensively in this study.

Typically, the mechanical response of viscoelastic materials is history-dependent, and to account for that, time-dependent behaviors of polymers were expressed as a function of reduced time ($\xi$), which can be expressed as [32]

$$\xi = \frac{t}{a_T}$$  \hspace{1cm} (30)$$

Therefore,

$$E_T(t) = E_{T_o}(\xi = \frac{t}{a_T})$$  \hspace{1cm} (31)$$

where $t$ is the time, and $a_T$ is the shift factor.

Experiments were designed to study the time-temperature-dependent (TTD) behaviors of UD and PW prepreg laminates. UD panels of 50mm×50mm and 2-ply thickness were fabricated at four distinct cure states while the same size PW panels were fabricated at fully cured state
only. Figure 28 shows three different time periods of the dwell stage from where the cure cycle was discontinued. Here the subscript represents the time in minutes from the beginning of dwell time (i.e., $t_{55}$ means that the cycle was stopped at 55$^{th}$ minute of dwell cycle). Specimens were prepared from these laminates with 0, 45, and 90 degree fiber directions of the laminate.

![Figure 28 Time periods of the cure cycles used to obtain different states of cure](image)

Before starting the TTS experiments, LVR and $T_g$ of the corresponding cure states were determined to keep the deformation within the viscoelastically linear region and the temperature below the $T_g$, respectively. Specimens were equilibrated at 30 ºC for 10 minutes to achieve uniform temperature distribution throughout the furnace. A constant strain of 0.1% was applied as soon as the sample achieved thermal equilibrium and was then allowed to displace for 60 minutes. Following the displacement, the temperature was increased by 10 ºC repeatedly until the temperature reached the predetermined set point temperature. Figure 29 shows the typical thermal cycle of TTSP experiments. Depending on the $T_g$ or cure state of the specimens, the
length of experiments varied from 700 to 1100 minutes. Data collected using this method was used as the raw data and were analyzed by using TA Rheology Advantage Data Analysis software to construct the master curves.

Figure 29 Thermal cycle of a typical TTS experiment
CHAPTER 4
RESULTS AND DISCUSSION

4.1 Thermal Analysis

Figure 30 shows thermal cycle utilized to obtain the change of cure state throughout the processing cycle of UD material. It is observed from the heat flow profile that the majority of crosslinking reactions take place during isothermal cure. At the beginning stage, the reaction rate reaches its peak magnitude. As time goes on, the rate of reaction decreases before reaching a plateau. To verify the completeness of chemical reactions, two consecutive dynamic scans are performed by heating the specimens from 25 °C to 290 °C. The dynamic scans reveal whether the reaction is incomplete after curing the specimen at 177 °C for 500 minutes; the remaining heat of reaction, commonly referred as residual heat of reaction, is determined from the dynamic scans. A comparison of the heat flow profiles for both dynamic scans (see Figure 31) shows that there is no heat of reaction left after the first dynamic scan. Therefore, the material is fully cured.

Baselines for the heat flow curve are frequently used to facilitate DOC calculation during cure. In this study, the baselines for ramp and dwell stages are chosen as the horizontal lines that coincide with the plateau region of the corresponding heat flow curves. However, the baseline for the residual heat flow curve is obtained by joining its plateau regions using a straight line as described in Figure 31. The ultimate heat of reaction \( (H_U) \) is obtained by integrating the area enclosed by the exothermic heat flow curves and the corresponding baselines. Utilizing the ultimate heat of reaction, the DOC during cure is obtained by following the procedure described in section 3.2.2. Figure 32 shows the DOC profile for the UD material during cure, and the fit with the Springer-Loos model. The model fits very well with the experimental results.
### TABLE 3

**FITTING PARAMETERS OF SPRINGER-LOOS MODEL**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>8.20E+04</td>
<td>J/mol</td>
</tr>
<tr>
<td>E2</td>
<td>2.64E+04</td>
<td>J/mol</td>
</tr>
<tr>
<td>A1</td>
<td>1.20E+04</td>
<td>1/sec</td>
</tr>
<tr>
<td>A2</td>
<td>-2.19E-03</td>
<td>1/sec</td>
</tr>
<tr>
<td>B</td>
<td>6.60E+03</td>
<td>-</td>
</tr>
</tbody>
</table>

---

**Figure 30** Heat flow curve for the extended MRCC to achieve the complete degree of conversion of UD material
Figure 31 Residual heat of reaction for two consecutive dynamic scans

Figure 32 DOC profile of IM7/977-2 UD during cure for manufacturer’s recommended cure cycle (MRCC)
4.2 Stress Relaxation during Cure

The stress relaxation (SR) behavior of IM7/977-2 UD during cure was studied from the time of gelation ($t_{gel}$). To identify the approximate time of gelation for the proposed cure cycle, fiber directional samples were prepared and studied in the DMA in strain controlled mode by applying an oscillating strain of 0.01%. Figure 33 illustrates the complex viscosity ($\eta^*$) and Tan delta ($\delta$) profiles obtained from the experiments. The data shows that the onset of the exponential increase of complex viscosity takes place at approximately the 20th minute of dwell stage.

![Figure 33 Complex viscosity ($\eta^*$), tan delta ($\delta$), and temperature vs. time of MRCC.](image)

4.2.1 Cure State of the Material

Only the fiber direction of the prepreg can carry the load while the resin is still in the B-stage. Therefore, the SR behavior for the entire isothermal cure stage was studied for fiber directional specimens (20mm×2mm×0.25mm) only. Figure 34 shows the SR behavior of UD tape in the fiber direction during cure. Due to the applied strain, the relaxation modulus reaches...
to certain magnitude at the beginning stage of the experiment. Following that, a typical relaxation behavior is observed for 10-15 minutes. After plateauing, it starts to increase again, which is unusual compared to traditional relaxation behavior. A close observation of the phenomenon shows that this transition occurs roughly at the time of gelation, which is confirmed by plotting the relaxation data against the degree of cure (DOC). This transition happens at the cure state of $\alpha \approx 0.45 - 0.5$. It is found that the excessive rate of crosslinking reactions accelerates the evolution of the mechanical modulus of the material; hence, the relaxation modulus starts to increase rather than staying at its plateau.

![Figure 34 Stress relaxation behavior of 977-2 UD during cure in the fiber direction](image)
To have a better understanding of this phenomenon, more investigation was performed by starting the SR experiments from the onset of dwell time to the 120th min of that stage, with a time gap of 20 minutes between each experiment. All of these secondary experiments were continued until the end of dwell time. For the benefit of illustration, a combined plot of results from different experiments has been shown in Figure 36. These results demonstrate that the peak relaxation modulus increases with the increase of degree of cure. A significant difference in stress relaxation behavior profiles is observed between the time $t_0$ and $t_{120}$, where $t_0$ and $t_{120}$ is the 0th and 120th minute of dwell time, respectively. Relaxation modulus profiles between $t_0$ and $t_{80}$ show a similar incremental trend of relaxation modulus as observed in Figure 34; whereas the experiments from $t_{100}$ to $t_{120}$ show a more conventional trend of SR behavior. At 100th minute of dwell time, the material approaches completion of its structural evolution process as confirmed by the onset of the plateau region of relaxation modulus in Figure 34. As a result, the material behaves more like fully processed material than a continuously changing material. SR modulus
behavior ahead of this period (i.e., $t_o$ to $t_{180}$) is greatly affected by accelerated cross-linking reactions. Therefore, the SR behavior during cure strongly depends on the cure status of the material.

Figure 36 Stress relaxation behavior of 977-2 UD started at different time period of isothermal cure stage

4.2.2 Storage Modulus versus Stress Relaxation Modulus

In order to study the stress relaxation (SR) modulus and storage modulus during cure, fiber directional specimens of the same size were prepared and the experiments were conducted using similar loading conditions. Figure 37 demonstrates the combined plot of storage modulus ($E'$) and SR modulus ($E(t)$) as a function of time. It shows that the profile of storage modulus and stress relaxation modulus during cure is quite similar except for the magnitude as the mechanical modulus of the material is always higher than the SR modulus. It indicates that the storage and relaxation modulus during cure originates from same physical phenomenon but expressed in different ways.
4.2.3 Fiber Directional Mismatch

To study the effect of directional mismatch of plies, specimens were prepared with a stacking sequence of $[0/\theta]$, where $\theta$ varied from 0 to 90 degrees with an increment of 15 degrees. Figure 38 shows that the peak stress relaxation modulus (PSRM) at the end of the cure cycle varies significantly with the change of stacking sequences even though the relaxation profiles for all the cases are similar. Figure 39 shows the plotting of PSRM values against the angle of ply orientation mismatch. Each PSRM value in Figure 39 represents an average of 2-3 repeating experiments.

Sources of variation of PSRM for different mismatch angles are embedded into two fundamental mechanical behaviors of specimens: (1) the proportion of the applied load shared by the fibers and (2) the deformability of the samples in the transverse direction. When the angle of ply orientation mismatch is zero (i.e., plies are parallel), the whole load is carried by the stiff carbon fibers of both plies. Comparatively, the in-plane transverse direction (second direction)
herein is much weaker than the fiber direction. Therefore, the specimen cannot deform in the first direction, but deforms considerably in the second direction. When the mismatch angle increases to 15 degrees (i.e., [0/15] stacking sequence), the bottom ply takes the maximum portion of the load, while the top ply faces the off-axis loading. However, the second direction of the specimen is still highly deformable; therefore, the overall stiffness of the specimen decreases significantly, which lowers the SR modulus as well. As the magnitude of the mismatch angle increases, the degree of dependency on the carbon fiber increases in the second direction. In the instance of extreme mismatch (i.e., [0/90] stacking sequence), both in-plane directions become fiber dominant. As a result, the deformation of the sample in both the first and second directions becomes limited due to the presence of reinforcing fibers. The stiffness of the sample increases with the increase of mismatch angles, which directly affects the stress relaxation modulus of the specimens as well.

Figure 38 Stress relaxation during cure measured for 2-layer laminates having different fiber orientations
Figure 39 Peak stress relaxation modulus during cure for different stacking sequences

### 4.2.4 Relative Position of the Plies

Figure 40 illustrates that the change of relative position of plies in the z-direction does not change the effective stiffness of the specimens, with respect to the neutral axis. In contrast to the UD specimens, however, they have quite low relaxation modulus. The discrepancy of these behaviors can be explained by eliciting the phenomena mentioned in section 4.2.3. Briefly, random change of ply positions does not change the proportion of fibers in the first and second directions of the laminates; thereby there is no change in mechanical behavior either. Rather, it lowers the number of 0 degree plies as compared to UD laminates. Taking pictures of the cured specimens, it is observed that even though the modulus is not significantly different for four laminates, the magnitude of distortion is different.
4.2.5 Stacking Sequence

Specimens were prepared from 3-ply laminates of UD prepreg with distinct stacking sequences. A noticeable variation in SR performance of the specimens was observed among four individual cases (see Figure 41); therefore, the source of this variation can be attributed to the lay-up sequence of the laminates. Figure 41 indicates that the [90/90/90] stacking sequence is highly deformable in the loading direction which is confirmed by the sample’s lowest relaxation modulus during cure. Conversely, the specimen with a [90/0/90] stacking sequence achieves the highest magnitude of relaxation modulus during cure. In section 4.2.3, Figure 39 describes this phenomenon partially when it illustrates that [0/90] orientation has relatively higher modulus due to its bidirectional reinforcement. [90/0/90] stacking sequence is an extension of the [0/90] sequence and is therefore stronger and stiffer than any other laminates under consideration. Similarly, the [0/45/90] and [45/0/-45] stacking sequences can be considered as the extension of the [0/45] orientation in Figure 39, with an extra ply of 90 and -45 degree orientation,
respectively. As expected, the 90 degree ply adds more stiffness to the specimen than the -45 degree ply. Therefore, it can be concluded that the stacking sequences of laminates can affect the relaxation behavior to a great extent.

![Graph showing stress relaxation behavior](image)

**Figure 41** Stress relaxation behavior of 3-ply laminates with different stacking sequences

### 4.2.6 SR Behavior in Three In-plane Directions of UD Laminates

SR behavior of UD laminates in three in-plane directions (0, 45, and 90 degrees) is shown in Figure 42. Experimental study clearly indicates that the relaxation modulus of an UD laminate is different in these directions, and thereby the relaxation of residual stress varies as well (see Figure 42). As expected, the fiber direction of UD laminate shows superior behavior than any other off-axis directions. On the other hand, strength of the laminate in the off-axis directions is strongly dependent on the modulus of resin and the behavior of the fiber/matrix interface under different loading conditions. In this study, the tension load applied to the specimen acts as transverse tensile load on the fiber/matrix interface of 90 degree fiber
directional specimens and as shear load on the 45 degree fiber directional specimens. The SR modulus of 45 and 90 degree samples show them to be very close to their magnitude in the early stages of the experiment, but the 90 degree sample gradually gains a higher modulus than the 45 degree sample. Since the modulus of the resin is similar for both samples, the behavior of the interface is most likely the cause of this variation (assuming that the fiber and resin are perfectly bonded at the interface). It has been reported in the literature that when the fiber/matrix interface undergoes shear loading, a frictional slippage between fiber and resin is one of the reasons that lowers down the shear modulus of the laminate when compared to the transverse modulus [59, 60]. Therefore, among the three directions, the 45 degree direction of the UD laminate has the ability to release higher residual stress.

![Figure 42 Stress relaxation of unidirectional laminate in 0, 45, and 90 degree fiber directions](image)

**Figure 42 Stress relaxation of unidirectional laminate in 0, 45, and 90 degree fiber directions**

### 4.2.7 Storage Modulus and SR Modulus: UD vs. PW

Before moving to the SR experiments, a comparative study was performed on the fiber directional modulus of both UD and PW prepregs. Here, Figure 43 shows that the mechanical
The modulus of UD material is always higher than PW material during cure, even though the type of carbon fiber and resin is same for both materials. It is believed that the distinct fiber arrangement of these two prepreg systems is the source of the variation in performance. In the PW fabric prepreg, the warp tow crosses the fill tow by going over the first, then under the second, and so on. After weaving like this, carbon fiber tows take a wavy shape along the length or width of the prepreg. When resin viscosity decreases during cure, wave shaped fibers attempt to straighten under the tension load applied from the DMA, which is not common for UD prepreg. Therefore, the UD prepreg is less deformable than the PW prepreg during cure and, as a result, it gains higher modulus than PW prepregs.

![Figure 43 Change of modulus of UD and PW prepregs during cure](image)

After gaining some knowledge about the mechanical modulus of these two prepregs, SR experiments were conducted during cure in 0 and 45 degree fiber orientations. Here, only 0 degree fiber orientation was chosen as the fiber arrangement and mechanical modulus in both 0 and 90 degree fiber orientations were found to be similar (see Figure 44) for this material. The
SR behavior of both UD and PW materials during cure has been plotted in Figure 45. Sample sizes and loading conditions were kept the same for both materials in order to allow for a valid comparison. Interestingly, the 45 degree fiber directional specimens of PW material were unable to take the load (strain of 0.01%) at the 20th minute of the isothermal cure cycle. Because of this early weakness, the experiment for PW prepregs was started at 40th minute of the isothermal cure stage.

However, the reasoning discussed earlier in this section for the lower storage modulus (\(E'\)) of PW materials during cure can be evoked here to explain the lower SR modulus of PW prepreg as well. Therefore, due to the waviness of fiber tows the PW specimens are much deformable than the UD specimens, regardless of their fiber orientations. The comparatively lower SR modulus of PW prepregs clearly states that the PW material will release higher residual stress than the UD material in these three directions, but in order to achieve that, a considerable portion of mechanical strength would need to be compromised.

![Figure 44 Development of modulus of PW fabric in two in-plane principal directions of the laminate](image)
4.3 Stress Relaxation of Cured Laminates

As previously mentioned in section 3.3.3.3, UD prepregs were cured at four distinct cure states while the fully cured laminates of PW prepreg were utilized to study the time-temperature-dependent behaviors. Figure 46 shows the duration of isothermal cure stage used to cure the panels and the corresponding states of cure of those UD laminates (i.e., $t_{55}$ indicates that the MRCC was terminated at 55th minute of dwell stage).
Figure 46 Termination times of manufacturer’s recommended cure cycles (MRCCs) to achieve desired degree of cure of UD laminates

4.3.1 Liner Viscoelastic Region (LVR)

DMA strain-sweep experiments were performed to determine the linear viscoelastic region (LVR) of both UD and PW materials. Figure 47 displays the normalized storage modulus profiles for both materials, which shows a descending pattern of storage modulus as a function of strain rates. Analyzing the experimental results for all the cases, a common strain rate of 0.1% was chosen for the TTS experiments which stay in the region of 95% or more of its initial magnitude. This common strain rate makes it easier to draw a sensible comparison between the relevant experimental results.
4.3.2 Glass Transition Temperature ($T_g$)

Specimens were prepared from both UD and PW materials to obtain the $T_g$, and the experiments were conducted in the DMA in strain controlled mode using an oscillating strain of 0.02%. Figure 48 shows the nonlinear increase of $T_g$ obtained at different cure states of UD materials.
4.3.3 Time-Temperature Superposition (TTS)

4.3.3.1 Basic Steps of TTS Analysis

Experiments were performed in the DMA by applying the TTS technique, to obtain the raw data required to construct the stress relaxation (SR) master curves. The collected raw data subsequently was used to construct the master curve, and the procedure to construct the master curves is presented here schematically in Figure 49, Figure 50, and Figure 51 by showing some representative data. They demonstrate the three major steps that are followed throughout the study to construct the master curves. Rheology Advantage Data Analysis, V5.7.0 (TA Instruments, New Castle, DE) Software is used to process the raw data.

Figure 49 demonstrates the first step of the master curve construction procedure, which is the collection of raw data from the TTS experiment. Experimental data indicated that the relaxation modulus decreases as the temperature increases. In other words, the composite materials become more deformable at relatively higher temperatures. Figure 50 represents the second step of the procedure, which shows the simplified experimental data against the same
logarithmic time scale for different temperatures. The final step is to construct the master curve by superimposing these individual curves (see Figure 50), as shown in Figure 51. In order to do that, the curve associated with 30 °C is chosen as the reference curve and rest of the curves are shifted along the reduced time ($\xi$) axis with respect to the reference curve. The inset graph in Figure 51 shows the behavior of logarithmic shift factors ($a_T$) as a function of temperature. It clearly indicates that one model is not enough to create a meaningful master curve for this material. Both Arrhenius and Linear model of shift factors are used to create a smooth master curve. Zarrelli et al. [32] observed similar behavior of shift factors in their study of relaxation of high-temperature epoxy. Interestingly, the same characteristic nature of shift factors ($a_T$) is observed for the whole TTS study in the off-axis fiber direction; therefore, the same principle is followed consistently for rest of this study.

Figure 49 Raw data of a TTS experiment performed on the 45 degree fiber direction specimen
Figure 50 SR behavior of UD laminate with 45 degree fiber direction at different temperatures
Figure 51 SR master curve of UD laminate as a function a reduced time, $\xi$ (s) in 45 degree fiber direction and the shift factors ($a_T$) as a function of temperature

### 4.3.3.2 Temperature Dependent Behavior

Based on the study of the previous section, an estimation of the long-term mechanical performance of UD laminates in 45 degree fiber direction was completed at different temperatures. Figure 52 shows the master curves for different reference temperatures ($T_{ref}$), where the reference temperature ($T_{ref}$) can be considered analogous to the operating temperature of the composite structures. Therefore, the prediction of the analytical study shows that the service temperature can significantly affect the mechanical performance of the PMCs. For instance, if the allowable limit of mechanical performance is considered to be 50% of its initial relaxation modulus, then it indicates that at 30 °C it takes more than 20 years to reach that limit,
while at 120 °C it takes less than an hour to reach the same stage. However, the loading condition in real service conditions can be even more complicated and can affect the performance to an even greater extent.

Figure 52 SR master curves at difference reference temperatures ($T_{\text{ref}}$)

4.3.3.3 Fiber Directions and DOC ($\alpha$) of the Laminate

Figure 53 shows the relaxation modulus master curve for 0, 45, and 90 degree fiber directions of the UD laminate at four distinct states of cure ($\alpha$) of the material. The same experimental procedure as described in the previous section was followed to create master curves for different experimental conditions. It is observed that the laminates show very insignificant stress relaxation behavior in the fiber direction; therefore, the relaxation behavior in the fiber direction is shown for the least cure state of the material only. On the other hand, the 45 and 90 degree fiber directional specimens relax completely if sufficient time is allowed. Interestingly,
the 45 degree fiber directional specimens show distinguishably faster SR behavior for all cure stages, which complies with the experimental results obtained for the same material during cure. Additionally, a persuasive difference in the rate of relaxation or the onset time of relaxation is observed among the cure states. In order to emphasize the effect of states of cure (\(\alpha\)), experimental results are plotted together in Figure 54 for samples with the same fiber direction at different cure states (\(\alpha\)). As Figure 53 illustrates, higher degrees of conversion prolong the time of complete relaxation, and vice versa.
Figure 53 Stress relaxation of UD specimens for different cure states of the material and different fiber orientations of same DOC
Figure 54 Relaxation modulus for four different DOCs of the laminate in the fiber direction of (a) 90 and (b) 45 degree
4.3.3.4 UD vs. PW Laminate

By following consistent experimental procedures, SR behavior of fully processed PW material is studied in this section. Figure 55 shows the SR master curve for PW material. Unlike the UD material, the two in-plane principal directions (0 and 90 degree directions) of the PW laminate are highly reinforced by the carbon fibers; therefore, the PW laminate is expected to display a similar kind of stress relaxation behavior in both directions. Relying on this assumption, only relaxation behavior in 0 degree fiber direction is shown here. Figure 55 demonstrates that the specimen shows negligible time-temperature dependent SR behavior in the 0 degree fiber direction while the 45 degree direction exhibits a considerable change in SR behavior.

![Figure 55 SR master curves of cured specimen of PW material](image)

Since identical experimental conditions were used for both UD and PW prepregs, the experimental results of fully processed materials of both kinds are plotted together in Figure 56.
to compare performance. Figure 56 shows a distinguishable variance between the time-temperature dependent behaviors of UD and PW materials. The PW laminate shows superior performance over UD laminate in 90 degree fiber direction, because of the presence of high strength carbon fibers in that direction. In 45 degree fiber direction, the PW laminate shows better performance over UD laminate, which directly opposes their relative performance during cure. The PW specimens show higher SR modulus and lower decay rate of relaxation modulus than the UD specimens. Interweaved carbon fiber tows of PW laminate is assumed to be the possible source of these specimens’ superior performance. Here, the carbon fiber tows are interlocked and have higher interfacial resistance than the UD prepreg which may account for the SR performance of PW prepregs in 45 degree fiber direction.

Figure 56 A comparative plot of SR modulus master curve of UD and PW laminates for different fiber directions
CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The objective of this study was to investigate the stress relaxation (SR) behavior of two commercial prepreg composites, IM7/977-2 unidirectional tape (UD) and IM7/977-2 plain weave fabric (PW), during and after cure. This research was primarily focused on the study of thermal and rheological behavior of the unidirectional (UD) material using the DSC and DMA, respectively, to understand the fundamental nature of the stress relaxation phenomenon as well as to study the factors that can affect SR behavior. The data obtained from UD material were then compared with the findings associated with the fabric (PW) material for the same experimental conditions in order to draw valid comparisons between them.

The conclusions are divided into two major subcategories:

- Stress relaxation during cure
- Stress relaxation after cure

**Stress Relaxation during Cure**

To investigate the SR behavior during cure, experiments were started at the approximate time of gelation of the resin. The exponential increase of the SR modulus at the gel point indicated that the stress relaxation behavior of thermosetting composite is strongly dependent on the cure state of the material. In another study it was observed that when the material approached the vitrification, stress relaxation was no longer affected by the slow crosslinking reaction rate of the material.

The similarity between the SR modulus and mechanical modulus profiles indicated that they originated from the same physical phenomenon, but expressed through different
mechanisms. It was found that the fiber directional mismatch and stacking sequence of the laminate could affect the relaxation behavior to a great extent, whereas the change of ply positions with respect to the neutral axis of the laminate did not affect the SR modulus. For unidirectional laminates, among 0, 45, and 90 degree fiber directions, the 45 degree fiber direction had the lowest SR modulus; therefore, the laminate was capable of releasing the highest amount of stresses in this direction.

A comparison of SR behavior between UD and PW materials demonstrated that even though the PW material has lower mechanical modulus as compared to the UD material, the PW laminate would produce less process-induced stress.

**Stress Relaxation after Cure**

Utilizing the time-temperature superposition (TTS) principle, SR behavior of cured laminates was studied to investigate the effects of combination of different factors: the fiber orientation of the specimen, cure state of the material, and two types of fiber arrangements of the prepreg. SR behavior for every combination of these factors was presented by the “master curve” of the SR modulus. Common experimental conditions were maintained for all TTS experiments to ensure valid comparisons within the findings.

Experimental data showed that the horizontal shift factors ($a_T$) for the off-axis directional master curves followed both Arrhenius and linear models as a function of temperature. A close observation of relaxation master curves at different temperatures indicated that the relaxation rate of composite laminate increased significantly as the service temperature increases.

A detailed study was performed to investigate the SR behavior of unidirectional laminate for the combinations of three fiber directions and four cure states of the material. The experimental results clearly indicated that the DOC of the laminate affects the SR behavior of the
laminate by prolonging the relaxation time at higher DOC, and vice versa. However, the rate of SR for 45 degree fiber direction material was higher than that at 90 degree fiber direction, though the rate difference became less significant as the DOC increased. Since the carbon fibers do not show any noticeable viscoelastic behavior, the laminate did not relax considerably in the 0 degree fiber direction.

Comparing the performance of UD and PW materials, PW material showed better performance in terms of SR behavior. Due to the presence of carbon fibers in both in-plane directions, PW automatically showed superior performance than the UD material in the in-plane directions. On the other hand, in the 45 degree fiber direction, the rate of change of relaxation modulus of PW laminate was lower than the UD material and the final relaxation modulus of the PW laminate was higher than the UD laminate.

5.2 Recommendations

- While this study focuses on the carbon fiber/epoxy prepreg composites only, it can be extended for prepreg systems having different fiber and resin types. A comparative study will show their relative relaxation performance at particular experimental condition.
- While conducting experimental study, the interaction between tool and the composites and the environmental pressure can be considered, to bring the experimental conditions as close as possible to the autoclave processing for thermosetting composites.
- Investigation on inter-ply and intra-ply stress relaxation behavior will help to achieve a better understanding of this phenomenon.
- Develop a constitutive model to describe the stress relaxation behavior of thermosetting composites during and after cure.
- Study the strain rate and environmental condition dependent stress relaxation behavior of prepreg composites.
- Investigate the stress relaxation behavior during cool down from the cure temperature.
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REFERENCES (Continued)


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