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Cure Cycle Design Methodology for Fabricating Reactive Resin Matrix Fiber Reinforced Composites

A Protocol for Producing Void-Free Quality Laminates

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Abstract

For the fabrication of resin matrix fiber reinforced composite laminates, a workable cure cycle (i.e., temperature and pressure profiles as a function of processing time) is needed and is critical for achieving void-free laminate consolidation. Design of such a cure cycle is not trivial, especially when dealing with reactive matrix resins. An empirical “trial and error” approach has been used as common practice in the composite industry. Such an approach is not only costly, but also ineffective at establishing the optimal processing conditions for a specific resin/fiber composite system. In this report, a rational “processing science” based approach is established, and a universal cure cycle design protocol is proposed. Following this protocol, a workable and optimal cure cycle can be readily and rationally designed for most reactive resin systems in a cost effective way. This design protocol has been validated through experimental studies of several reactive polyimide composites for a wide spectrum of usage that has been documented in the previous publications.

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Introduction

Building a large industrial autoclave is a multimillion-dollar investment. Composite fabrication of structural sub-components such as aircraft wings in autoclaves typically takes a long time with high cost. Many high performance resin/fiber composites are thermosets, meaning that material cycling/recovery is not possible once cured. Investment in both material and equipment for the fabrication of each part is very substantial. A robust, workable and optimized cure cycle is therefore desirable and crucial to ensure an end product with the intended quality of design in an efficient and cost effective fashion.

Most fiber reinforced polymeric composites contain reactive resin matrices. One example is the aromatic polyimide composites which are widely used in the aerospace and electronics industries. This class of material exhibits a high glass transition temperature (T_g), thermal and thermo-oxidative stability at elevated temperatures, superior chemical resistance and excellent mechanical properties. One of the major problem areas is its poor processability. In fully imidized forms, many are insoluble in most organic solvents and are usually only infusible at elevated processing temperatures. Consequently, in most applications, a precursor poly(amide acid) solution in a high boiling polar solvent must first be prepared and then converted thermally to a polyimide.

When exposed to heat and pressure (i.e., in a cure cycle) during laminate fabrication, the precursor poly(amide acid) will cure through chemical reactions, and form a cured material with significantly enhanced properties. During cure, however, reaction by-products are generated and, in the meantime, resin fluidity (inverse of viscosity) is dramatically diminished because of chain extensions and/or chemical cross-links among long chain molecules. This makes processing a very difficult and challenging task. These issues, if not accounted for and effectively mitigated, will result in voids inside the laminate, which are detrimental to the mechanical properties of the final consolidated parts.

The design of a workable cure cycle for a given resin/fiber composite is not a trivial endeavor, especially when dealing with reactive matrix resins. In practice, an empirical “trial and error” approach has commonly been used [1-2]. Such an empirical method has several drawbacks;

- an extensive parametric experimental program is usually required to determine the optimal cure cycle for a given material,
- a cure cycle found to be satisfactory for a given material under one set of conditions may not be valid under a different set of conditions, and

- this approach does not ensure that the composite is cured completely under the optimal conditions in the shortest amount of time.

The existing method is therefore deemed costly, time consuming, and inefficient for producing laminates with acceptable quality. An alternate “processing science” approach is proposed in this report along with examples in the following sections.

Cure Cycle Design

Cure cycles for composites with reactive resin matrices usually consist of two-step ramp-and-hold temperature and pressure profiles as shown in Figure 1, where t_B is the B-stage duration, T_B is the B-stage temperature, t_P is the time of temperature ramp to pressure application point, T_C is the final cure temperature, P is the pressure, and R is the heating rate from T_B to T_C . Temperature and the hold duration for each step are unique for a given composite system. The low temperature ramp-and-hold step (T_B and t_B) is called the B-stage in composite fabrication terminology. At this step, pressure is absent, and volatiles (i.e., solvent and reaction by-products) are free to escape via vacuum (V). The high temperature hold (T_C) is for final forced consolidation (via pressure P). In order to produce a void-free high quality laminate, the residual processability (i.e., resin fluidity remaining after the B-staging period) and force application temperature (i.e., T_C) during final cure must be thoroughly understood.

Several critical parameters in the two-step cure cycle shown in Figure 1 are therefore identified as:

- B-stage temperature (T_B) and duration (t_B);
- Consolidation temperature (T_C) and consolidation force application point (t_P). For reactive polyimide composites, the duration of T_C is usually at least 2 hours to achieve full cure.
- Temperature ramp rate, R , which is kept slow to ensure thermal uniformity.
- Minimum pressure, P , which is effective for consolidation.

Processability of composites with reactive resin matrices involves a balance between the degree of volatile depletion and the residual fluidity (i.e., after the B-stage) remaining in the matrix. When volatiles are not depleted adequately before the force consolidation step, voids are trapped in the laminate yielding inferior quality. On the other hand, excessive resin cure advancement, as a result of excessive B-stage conditions (i.e., in both T_B and t_B), will make the composite un-processable under moderate pressures. The kinetics of volatile diffusion through the liquid phase is strongly dependent upon resin chemistry, chemo-viscosity, temperature, and time duration. While the reactive resin matrix continues (yet slowly) to cure during the (low temperatures) B-stage period, the resin viscosity continues to increase and the composite processability suffers. In order to achieve a void-free laminate, the cure (molding) cycle must enable a sufficient percentage of volatiles depleted through the thermal B-stage period (in the absence of pressure) before force consolidation. In the meantime, an

appreciable degree of residual resin fluidity should remain after the B-stage, allowing infiltration of resin through fiber bundles within the composite, during the pressure consolidation period initiated at the latter stage (i.e., elevated temperatures) of the cycle. Such a balancing act between degree of residual volatiles and residual fluidity during composite fabrication is very complex and makes the design of cure cycles extremely challenging.

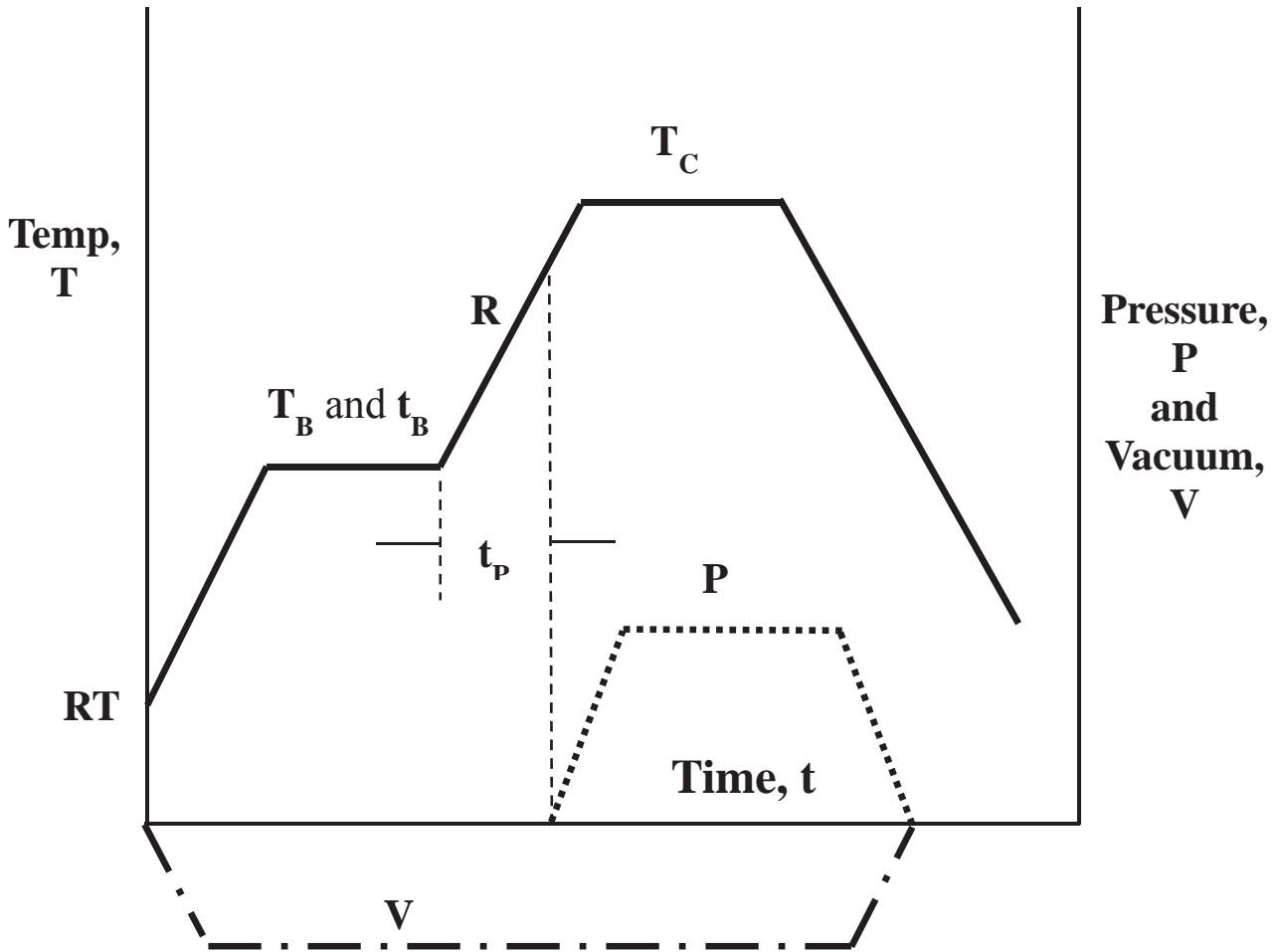


Figure 1. Schematic drawing of a typical two-step cure cycle profile.

Processing Science-Based Cure Cycle Design Protocol

Traditional “trial and error” approaches for cure cycle design as shown in Figure 1 employ parametric studies. This approach is simply too primitive, costly, time consuming and ineffective. A universal “processing science” approach using available analytical tools to

effectively measure and logically analyze and design a workable cycle for any given unique resin/fiber composite will bring much needed improvement for this critical fabrication issue.

In order to design a workable cure cycle for a given resin, four aspects of resin and composite properties have to be considered. They are volatile management, chemical curing kinetics, evolution of resin morphology, and residual processability after the B-staging period. With the aid of analytical tools and techniques, a “processing science” based cure cycle design methodology can be determined. The proposed design protocol consists of measuring volatile depletion mechanisms by thermal gravimetric analysis (TGA), measuring degree of thermally initiated reactions and the morphology of partially cured resins by differential scanning calorimetry (DSC), and measuring residual fluidity and on-set temperature for gelation of partially cured resins by melt rheometer. Based on these measurements, a workable molding cycle for a given resin composite system can be readily and logically designed.

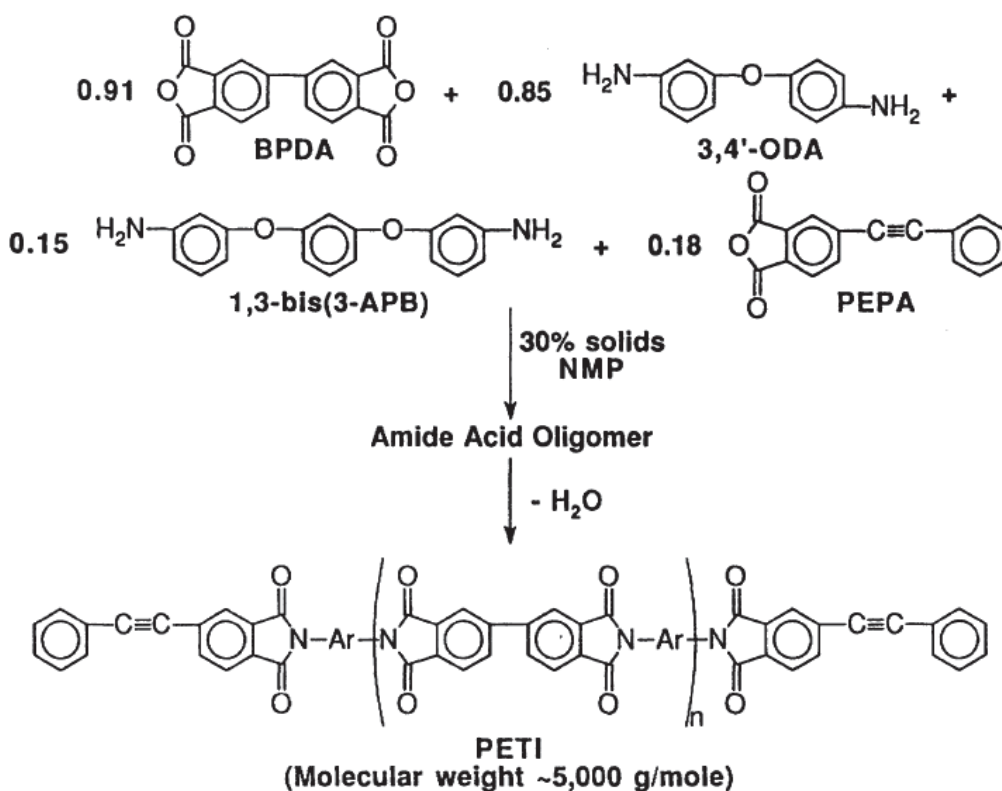


Figure 2. Synthesis of PETI

In the following, fabrication of LARC™-PETI5 polyimide composite, in the precursor form of LARC™-PETI5/NMP poly(amide acid) solution, is used as an example to illustrate the proposed design protocol. The synthesis of PETI is shown in Figure 2. A slurry of the appropriate amounts of BPDA (3,3',4,4'-biphenyltetracarboxylic dianhydride) and PEPA (4-

phenylethynylphthalic anhydride) was added to a solution of the 3,4'-ODA (3,4'-oxydianiline) and APB (1,3-bis (3-aminophenoxy)benzene) in NMP (*N*-methylpyrrolidinone solvent) at 23°C under nitrogen. PEPA is the endcapper. Additional NMP was used to completely transfer the slurry to the reaction vessel and to obtain a 30% w/w solution. The amber solution was stirred at ambient temperature for 24 hrs under nitrogen. The selected stoichiometric imbalance of ~ 9% in favor of diamine resulted in a theoretical number average molecular weight of ~ 5,000 g/mol. The 30% (w/w) oligomeric amide acid solutions, as synthesized, were stored under nitrogen at - 40°C until use. To obtain PETI, a mixture of toluene and NMP was added to the stirred oligomeric amide acid solution and the solution was subsequently refluxed for 24 hrs. Upon removal of the toluene, with a Dean-Stark trap, the resulting cooled slurry was poured into water to precipitate a light yellow powder. The powder was washed with warm methanol and dried under vacuum at 225°C for 4 hrs to yield PETI [3].

Volatile Management

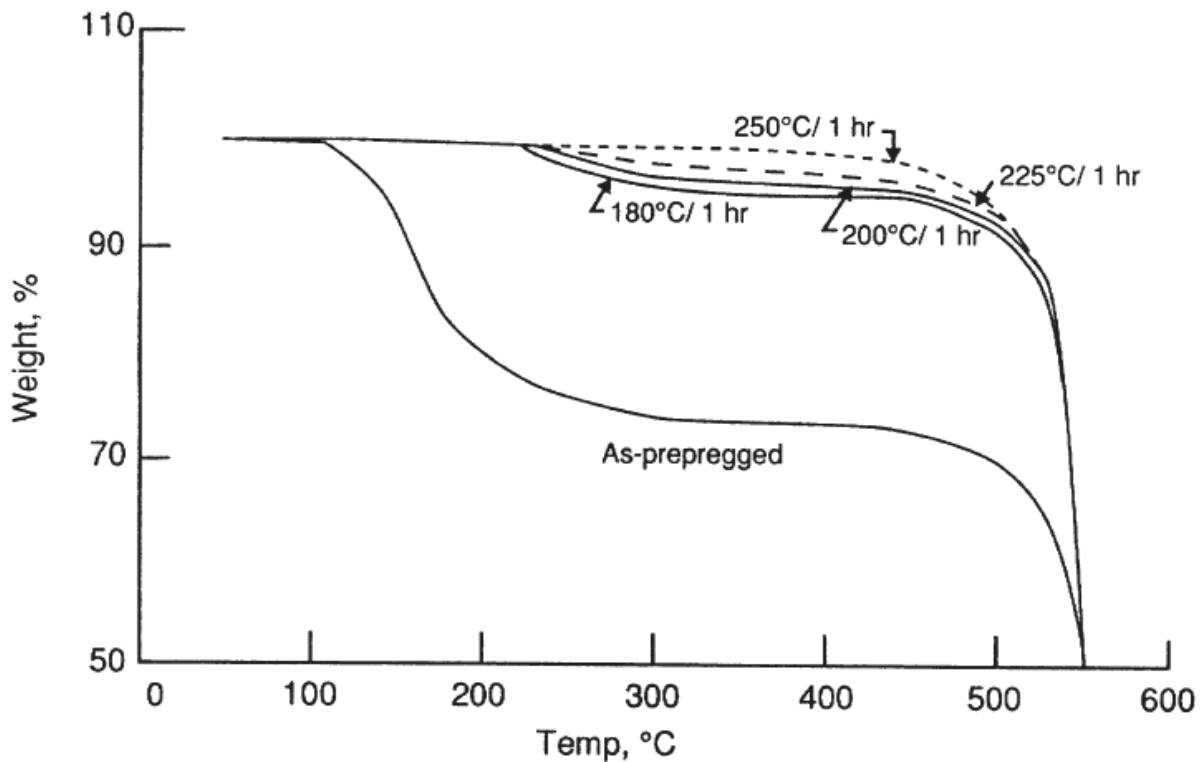


Figure 3. Weight loss behavior for oligomeric amide acid

Volatile management is accomplished through the design of an adequate B-stage profile. TGA is used to study volatile depletion mechanisms. In this analysis, resin specimens are taken from the prepreg flesh to preserve its thermal history during the prior prepreg manufacturing processes via the NASA Langley multipurpose prepreg machine [4-5]. Specimens are first pre-treated in an oven at several selected thermal conditions, i.e., T_B

and t_B , which include the estimated range of the (low temperature) B-stage condition. TGA measurements were performed on a Seiko TG/DTA 220 at 2.5°C/min in flowing (40 ml in nitrogen). Weight loss profiles were recorded.

Weight loss behavior was shown in Figure 3 and summarized in Table 1. The results indicated that the as-collected PETI5 poly(amide acid)/NMP flesh specimen contained 27% w/w residual NMP. Most of the solvent and reactive by-products were depleted after 250°C/1 hr pre-treatment, which resulted to a residual solvent of 0.2% w/w. A residual volatile level of < 0.5% w/w level was previously established, from prior experience, to be adequate for yielding composite laminate with less than 2% v/v void content [6-18]. The 0.2% w/w residual solvent content could be further reduced to zero by more severe B-stage conditions (i.e., 275°C/1 hr and 300°C/1 hr) as seen in Table. However, under these conditions, higher degree of imidization reactions shall bring the resin closer to full cure. Subsequent processability would then suffer due to the severe loss of resin fluidity. Based on these results, the 250°C/1 hr was identified as the preferred B-stage condition for this resin.

Table 1. Volatile depletion behavior for LARC™-PETI5/NMP specimen.

Thermal Pre-treatment Condition	Residual Volatile % w/w after Pre-treatment
As-collected (from prepreg)	27.0
180°C/1 hr	5.5
200°C/1 hr	4.6
225°C/1 hr	1.7
250°C/1 hr	0.2
275°C/1 hr	0
300°C/1 hr	0

Degree of Cure and Resin Morphology

Thermal properties such as the degree of cure (i.e., kinetics of chemical reaction) and morphology of the B-staged resins are next studied by DSC. Similarly, resin specimen was taken from the prepreg flesh to preserve its prior thermal history. Specimens were subjected to identical B-stage treatments as described in Table 1. DSC measurements were performed on a Shimadzu DSC-50 calorimeter at 10°C/min in nitrogen. Properties such as the glass transition temperature, T_g , the crystalline melting temperature, T_m , and endothermic heat, ΔH , were obtained. The results were shown in Figure 4, and tabulated in Table 2.

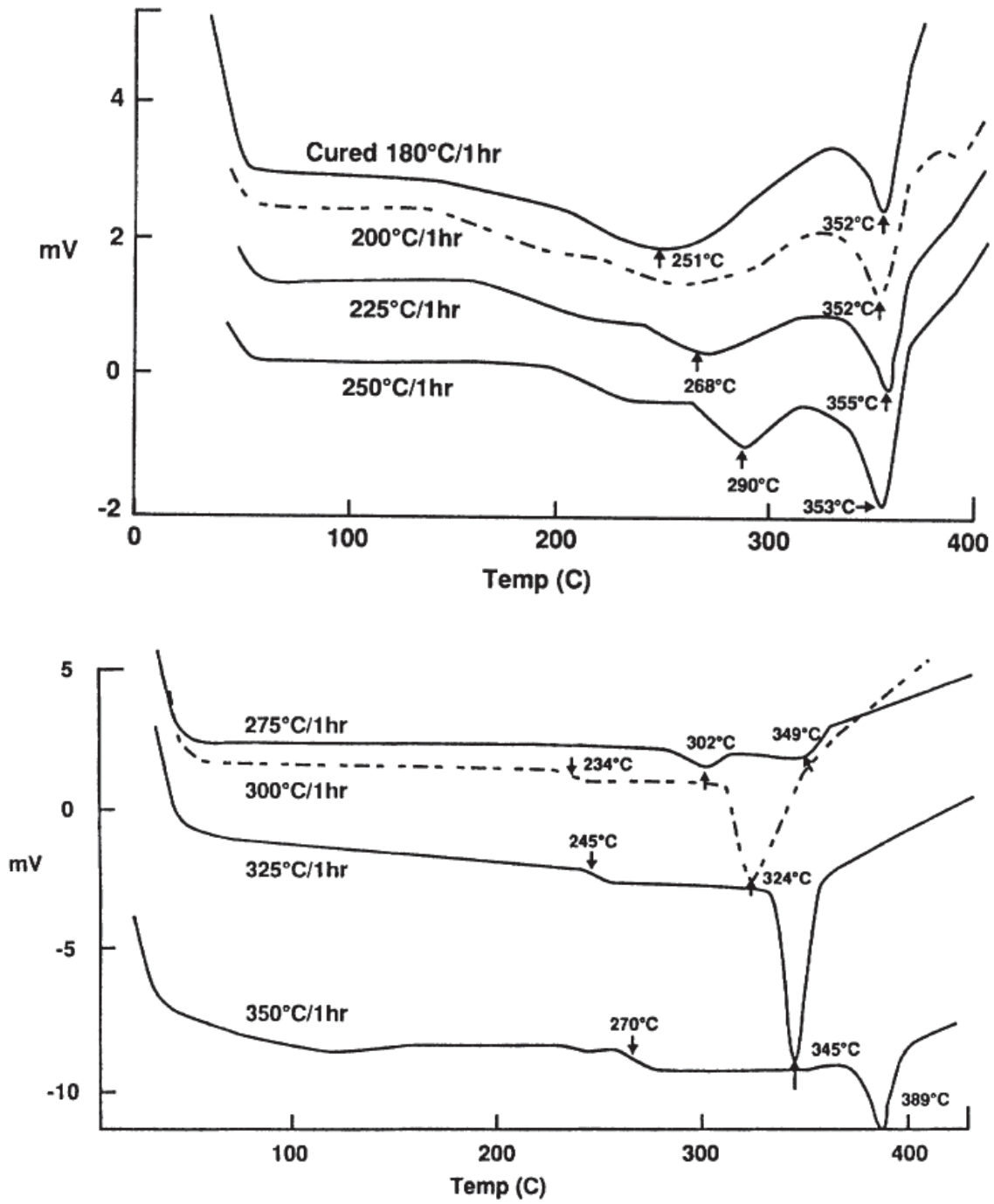


Figure 4. Crystalline melting behavior of thermally pre-treated PETI specimens with B-stage conditions indicated

Table 2 showed that, after the B-stage thermal treatments, all LARC™-PETI5/NMP specimens became semi-crystalline, which exhibited either single or double crystalline melting endothermic peaks. The 250°C/1 hr B-stage resulted in a semi-crystalline partially cured resin with a $T_g = 210^\circ\text{C}$, $T_m = 290^\circ$ and 353°C and $\Delta H = 21.5 \text{ J/g}$. The $T_g = 210^\circ\text{C}$ was 60°C below the nominal T_g attainable in a fully cured LARC™-PETI5/NMP resin, 270°C .

Table 2. Thermal properties of B-staged LARC™-PETI5/NMP*

Thermal Treatment	LARC™-PETI5/NMP (amide acid/NMP precursor)		
	T_g ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	ΔH (J/g)
180°C/1-hr	---	352	12.7
200°C/1-hr	---	352	12.0
225°C/1-hr	---	268, 355	11.3
250°C/1-hr	210	290, 353	21.5
275°C/1-hr	220	302, 349	10.0
300°C/1-hr	234	324	38.6
325°C/1-hr	245	345	32.3
350°C/1-hr	270	389	13.7

*Semi-crystalline material after B-staged thermal pre-treatment indicated.

These results indicated that the 250°C/1 hr B-staged specimen exhibited a low degree of cure (a low T_g) with semi-crystalline morphology, which showed a high 353°C crystalline melting temperature. In order to produce a fully cured laminate with an amorphous resin matrix, the final consolidation temperature should be higher than 353°C . DSC measurements examined here provided crucial information to help select the final consolidation temperature for a given resin system.

Consolidation Pressure and Pressure Application Point

The third aspect of cure cycle design is the resin infiltration mechanism inside the fibrous preform during the final step of composite consolidation. Darcy's law of fluid flow through a porous media is the predominant mechanism, and therefore, need to understand the viscoelastic properties of the B-staged resins. Again, LARC™-

PETI5/NMP amid acid precursor is used as an example for illustration purposes. Measurements were conducted in Rheometric System 4. Thermally pre-treated PETI5 powder specimen was press molded at RT into disk form with 2.54 cm in diameter and approximate 1.5 mm in thickness. The compacted resin disk was then loaded between the parallel-plate fixture. The top plate was oscillated at a fixed strain of 5%, and an angular frequency of 10 rad/sec, while the lower plate was attached to a transducer which recorded the resultant torques. The torques were decomposed into in-phase storage modulus, G' , and out-of-phase loss modulus, G'' , as a function of time and temperature.

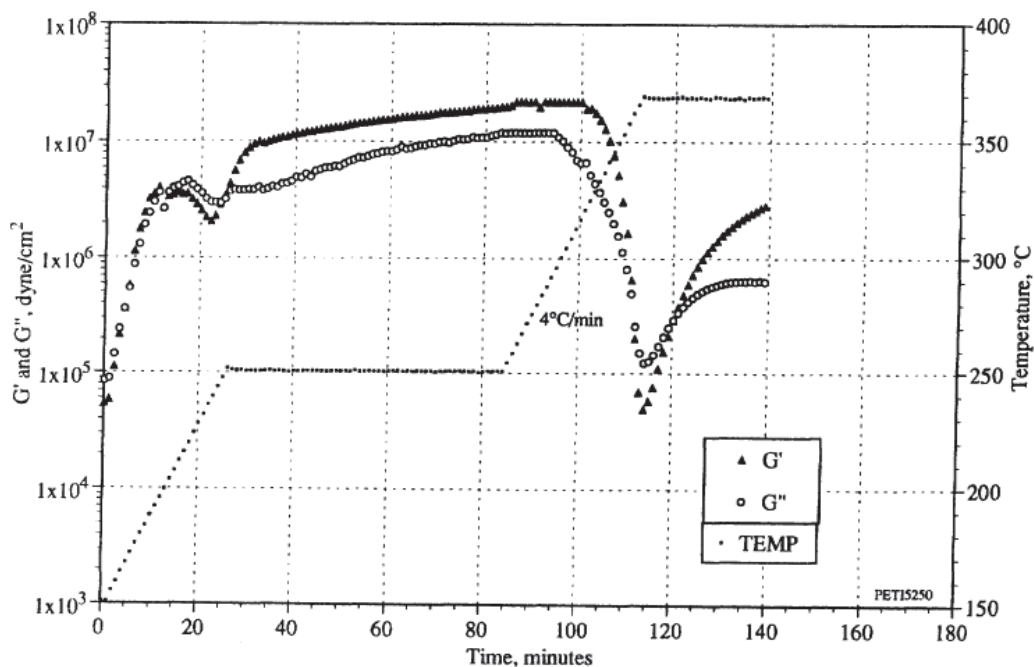


Figure 5. Storage (G') and Loss (G'') moduli of PETI under the two-step cure cycle indicated

Figure 5 showed results of measurement under a two-step ramp-and-hold temperature profile: temperature ramp at 4°C/min from 150°C to 250°C and hold for 60 mins; followed by a second ramp to 371°C and hold for 30 mins. Both G' and G'' were recorded. The temperature profile was the optimal design, based on the results of TGA and DSC analyses discussed above, to simulate the cure cycle for this resin system.

During the initial ramp period, values of G' and G'' increased with rising temperatures. This increase in moduli was an artifact and was attributed to the enhanced resin-metal interfacial bonding strength developed from the softening of the specimen. Slowly increase in moduli during the 250°C/1 hr hold period indicated a slow rate of imidization reaction at the temperature, and the material remained solid-like because G'

> G'' . Crystallites with two endothermic peaks at 290 and 353°C, respectively, were created during the thermal annealing in this period as discussed in Figure 4 and Table 2.

A sharp drop in moduli occurred during the second ramp from 250 to 371°C and the specimen turned to liquid-like with $G'' > G'$. The drop was attributed to the crystalline melting in specimen, as the melting started at ~ 290°C near the lower melting T_m and also cover the higher 353°C peak crystalline melting temperature (see Table 2). After melting, the moduli continued to decrease until a minimum of 1.2×10^5 dyne/cm² in G'' was reached at 371°C. The minimum moduli were converted to a complex viscosity of 2.8×10^4 Poise. In less than 10 mins into the 371°C hold, crosslinking reactions were triggered as manifested by formation of a gelation point where $\tan \delta = 1$ (i.e., $G' = G''$), and the specimen was transformed quickly to viscoelastic solid-like form with decreasing values of $\tan \delta$ (or $G' > G''$). Resin fluidity was diminished quickly at the same time.

Table 3. Viscoelastic properties of B-staged LARC™-PETI5/NMP.

Thermal Pre-treatment	LARC™-PETI5/NMP (amide acid precursor)		
	η_{\min} (10^4 Poise)	T_{η} (°C) at $\tan \delta_{\max}$	Δt (min) in which $\tan \delta > 1$
180°C/1-hr	2.5	364	5
200°C/1-hr	5.3	364	5
225°C/1-hr	2.8	364	5
225°C/2-hr	1.3	364	5
250°C/1-hr	2.8	364	5
250°C/2-hr	2.5	364	5
275°C/1-hr	2.2	364	5
300°C/1-hr	1.5	364	5

Rheological properties were tabulated in Table 3 for specimens subjected to the same thermal pre-treatments and used in TGA and DSC measurements discussed before. In Table 3, η_{\min} was value of the minimum viscosity; T_{η} was the temperature where the minimum viscosity was reached; Δt (mins) was the time period in which the resin remained viscoelastic liquid-like (i.e., $\tan \delta > 1$) behavior. For the 250°C/1 hr B-staged specimen, a semi-crystalline partially cured resin was resulted with $T_{m, \max} = 353^\circ\text{C}$

measured by the DSC in Table 2. Rheological measurements yielded $\eta_{\min} = 2.8 \times 10^4$ Poise at $T_{\eta} = 364^{\circ}$. T_{η} was found to be higher than the $T_{m, \max}$. This was expected, since η_{\min} tended to occur near $T_{m, \max}$ where the melting of the crystallites would aid in resin fluidity.

As shown in Table 3, the resin viscosity η_{\min} (i.e., inverse of residual fluidity) varied but remained in quarter order of magnitude range in values among various thermally pre-treated specimens. This was attributed to their semi-crystalline morphology created when subjected to the prior thermal pre-treatments period as discussed in Table 2. Crystalline was formed from low molecular weight imide oligomers. These oligomers, being locked-down in the crystalline micro-structures, were prohibited from further imidization reactions and/or chain extensions until melting occurred at elevated temperatures. The minimum viscosity was observed to occur at the same temperature (364°C) for all specimens.

The time period in which the resin remained viscoelastic liquid-like (i.e., $\tan \delta > 1$) was the same, 5 mins, suggesting that the processing window was very narrow for this resin system. Pressure in the laminate fabrication of LARC™-PETI5/NMP could be applied at the end of $250^{\circ}\text{C}/1$ hr B-stage period in Figure 5. This pressure application point would offer two advantages: 1) severe porosity formation within the laminate was unlikely to occur because of the low content of residual volatiles remained (0.2% w/w seen in Table 1), and 2) full residual resin fluidities would be utilized for the desired resin infiltration in the laminate during the second ramp-up and hold period. The residual viscosity level (i.e., 2.8×10^4 P) measured in Table 3 was moderate, suggesting, from experiences, that a moderate pressure (i.e., < 1.73 MPa or 250 psi) is adequate to consolidate the LARC-PETI5/NMP composite at a temperature $T_c > 364^{\circ}\text{C}$.

The proposed protocol for cure cycle design was summarized below:

- Determination of the extent of volatiles depletion:
Thermal Gravimetric Analysis (TGA) is used to probe the neat resin volatile depletion mechanism. Resin specimens, preferably taken from the prepreg flesh to preserve the thermal history during the prior prepreg fabrication process, are measured isothermally under several pre-determined temperature-time profiles. Resultant weight loss profiles are recorded. These weight loss profiles describe the volatile depletion behavior during the B-stage period.
- Determination of the curing behavior and evolution of resin morphology:
Differential Scanning Calorimeter (DSC) is used to probe the kinetics of chemical reactions and changes of morphology during resin curing. Resin specimens, after being subjected to the identical thermal pre-treatments as above, are measured under a specified heating rate. Advancement of the glass transition temperature and formation of crystalline structures are determined. These results help to determine the consolidation temperature in the second (higher temperature) hold step of the cure cycle.

- Determination of the consolidation pressure cycle:
Rheometry is used to probe the viscoelastic properties of the B-staged matrix resin. B-staged specimens are measured under several two-step ramp-and-hold temperature profiles. Residual resin fluidity after B-stage, minimum viscosity at temperature, and the gelation points can be determined from these measurements. These results will help in the determination of residual processability and the force application point in temperature and time for the final consolidation.

This cure cycle design protocol had been successfully applied to a number of polyimide matrix resins for the fabrication of composites, which were documented in References [3, 6-18].

Flow Diagram of the Design Protocol

A practical flow diagram for adapting the proposed cure cycle design protocol is shown in Chart 1. This design flow diagram involves an iteration scheme which ends with an optimal cure cycle for a given reactive resin system. The decisions points are science-based, as opposite to the practice of empirical reasoning.

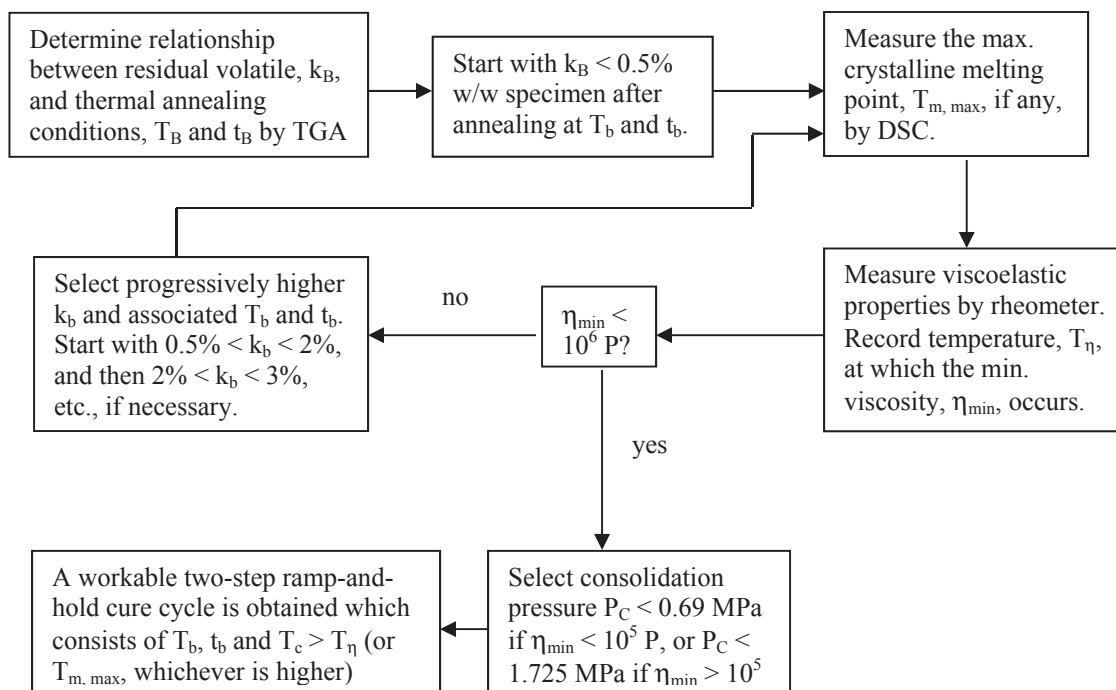


Chart 1. Flow diagram of the protocol for the cure cycle design methodology. K_B , residual volatile % w/w after the B-stage; P, viscosity unit in Poise; P_C , consolidation pressure in MPa; T_B , B-stage temperature; T_B , B-stage duration; T_C , consolidation temperature; $T_{m, max}$,

maximum crystalline melting temperature; T_{η} , temperature at which minimum viscosity occurs; η_{\min} , minimum viscosity in P.

As shown in Chart 1, several design criteria are established during the iterations. An optimal cure cycle could be reached by just one iteration if the following criteria are met: a) the residual volatiles after B-stage are $< 0.5\%$ w/w; b) the forced consolidation temperature is $T_c > T_{m, \max}$ (or T_{η} , whichever is higher); and c) the residual minimum viscosity is $\eta_{\min} < 10^6$ Poise. In the situation where $\eta_{\min} > 10^6$ Poise, a second iteration is needed by employing a less severe B-stage condition. This condition results in higher residual volatile content after B-stage, but enhances residual resin fluidity as well through the plasticizing effect. Consequently, η_{\min} becomes lower (i.e., $< 10^6$ Poises) affording a moderate pressure (i.e., < 1.725 MPa or 250 psi) for final consolidation. If additional volatile depletion is necessary, the pressure application point can be delayed until T_{η} , which is reached during the second temperature ramp.

When the design criteria cannot be met concurrently at the 5% w/w residual volatile level, the resin/fiber system is considered un-processable under moderate pressures. Void-free laminate parts cannot be fabricated. Refinement of the cure cycle is possible by narrowing the B-stage pre-treatment conditions in the TGA, DSC and rheometry analyses.

Conclusions

A typical two step cure cycle profile in composite fabrication has been reviewed. Critical processing parameters for a workable cure cycle, such as temperature, temperature hold duration, heating rate, and pressure application point, are identified. The interactions among these parameters in producing near void-free composite parts are critically discussed.

In the composite fabrication for a given resin matrix system, a cure cycle design based on parametric studies, i.e., the “trial and error” approach, has been commonly employed. Such an approach is simply too primitive, too costly, too time consuming and ineffective in reaching the optimal design of the cure cycle. An alternate “processing science” approach has been proposed in this report. The proposed approach utilizes common laboratory analytical devices to measure the thermal and rheological properties of the resin during cure. From these properties, a workable cure cycle can readily be obtained. The design protocol consists of measuring volatile depletion mechanisms by TGA, measuring degree of imidization reactions and the morphology evolution of partially cured resins by DSC, and measuring residual fluidity and on-set temperature for gelation of the partially cured resins by melt rheometry.

The effectiveness of the proposed design methodology has been demonstrated successfully to design the cure cycle for the poly (amid acid) LARC™-PETI5/NMP matrix resin solution system. The proposed methodology has also been applied successfully to many other poly

(amid acid) resin systems such as LARC™-ITPI, LARC™-8515, LARC™-IA, LARC™-IAX, LARC™-IAX2, LARC™-IAX3, LARC™-SCI, LARC™-RP46, LARC™-SI, LARC™-MPEI-1 [6-16].

Applying this cure cycle design methodology to the fabrication of composites with reactive matrix resin systems will reduce uncertainties and afford the designer an objective approach in reaching the optimal cure cycle, with confidence, for a given resin system.

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14. ABSTRACT For the fabrication of resin matrix fiber reinforced composite laminates, a workable cure cycle (i.e., temperature and pressure profiles as a function of processing time) is needed and is critical for achieving void-free laminate consolidation. Design of such a cure cycle is not trivial, especially when dealing with reactive matrix resins. An empirical "trial and error" approach has been used as common practice in the composite industry. Such an approach is not only costly, but also ineffective at establishing the optimal processing conditions for a specific resin/fiber composite system. In this report, a rational "processing science" based approach is established, and a universal cure cycle design protocol is proposed. Following this protocol, a workable and optimal cure cycle can be readily and rationally designed for most reactive resin systems in a cost effective way. This design protocol has been validated through experimental studies of several reactive polyimide composites for a wide spectrum of usage that has been documented in the previous publications.					
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