

## Processing Robustness for A Phenylethynyl Terminated Polyimide Composite\*

T. H. Hou  
NASA Langley Research Center, Hampton, Virginia 23681-0001

### ABSTRACT

The processability of a phenylethynyl terminated imide resin matrix (designated as PETI-5) composite is investigated. Unidirectional prepregs are made by coating an *N*-methylpyrrolidone solution of the amide acid oligomer (designated as PETAA-5/NMP) onto unsized IM7 fibers. Two batches of prepregs are used: one is made by NASA in-house, and the other is from an industrial source. The composite processing robustness is investigated with respect to the prepreg shelf life, the effect of B-staging conditions, and the optimal processing window. Prepreg rheology and open hole compression (OHC) strengths are found not to be affected by prolonged (i.e., up to 60 days) ambient storage. Rheological measurements indicate that the PETAA-5/NMP processability is only slightly affected over a wide range of B-stage temperatures from 250°C to 300°C. The OHC strength values are statistically indistinguishable among laminates consolidated using various B-staging conditions. An optimal processing window is established by means of the response surface methodology. IM7/PETAA-5/NMP prepreg is more sensitive to consolidation temperature than to pressure. A good consolidation is achievable at 371°C (700°F)/100 Psi, which yields an RT OHC strength of 62 Ksi. However, processability declines dramatically at temperatures below 350°C (662°F), as evidenced by the OHC strength values. The processability of the IM7/ LARC<sup>TM</sup> PETI-5 prepreg was found to be robust.

Key Words: Composites, Curing of Polymers, Polyimides, Voids

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## 1. INTRODUCTION

In 1989, NASA initiated the High Speed Research (HSR) program with the U.S. aerospace industry to develop technology for a Mach 2.4 High Speed Civil Transport (HSCT) plane. At Mach 2.4, the surface temperatures of the airplane would reach about 160°C (320°F). As a safety margin, the program required materials to perform at 177°C (350°F) for 60,000 hours. In addition to this long-term durability requirement, the candidate matrix resin and composite must exhibit no toxicity, high mechanical properties over the temperature range -54 to 177°C, resistance to moisture and solvents, no microcracking under thermal cyclings, acceptable handleability, robust processability under pressure < 1.4 MPa (200 Psi) and temperature < 370°C (700°F), and amenability to different fabrication processes, e.g., automated tape placement and autoclave curing, etc.. A resin designated LARC™ PETI-5 was selected as the candidate material for scale-up in HSCT airframe application. LARC™ PETI-5 is an imide oligomer terminated with phenylethynyl groups. It displayed an attractive combination of properties demanded by the HSCT both as adhesive and composite matrix [1-7].

LARC™ PETI-5 was primarily synthesized as an oligomeric (amide acid) solution in *N*-methylpyrrolidone (NMP), designated herein as PETAA-5/NMP. Like many polyimides, the PETAA-5/NMP system releases a reaction by-product (water) during the imidization reaction. Unidirectional IM7/PETAA-5/NMP wet prepreg contained about 22% w/w volatiles (NMP solvent and reaction by-product water). It is well documented that volatile management in polyimide composite fabrication is a critical and challenging issue. In order to achieve void-free quality laminates, volatiles have to be depleted before applying consolidation pressures. However, the boiling point of NMP (~200°C) falls within the temperature range (150° - 300°C) of the imidization reactions. Any attempt to deplete the carrier solvents from the composites will lead to a higher melt viscosity in the matrix resin. During the HSR, a molding cycle that includes 250°C/1 hr B-stage and 371°C/1 hr with 200 psi consolidation was successfully designed for the IM7/PETAA-5/NMP prepreg system. Void-free laminates with sizes up to 12" x 12" and 24 plies were fabricated with very good mechanical properties reported [7]. For these small parts, the imidization and (minimal, if any) crosslinking reactions occurring in the PETAA-5/NMP matrix during the 250°C/1 hr B-staging period did not compromise matrix resin processability to an unacceptable level.

In the manufacturing of the larger and thicker composite parts in an autoclave, a nonuniform part temperature distribution exists at any given time during the curing cycle. Consequently, nonuniform distributions in the degree of imidization result within the resin matrix. The volatile depletion mechanism may be distorted and composite processability be compromised. In addition, loss of tack in the prepreg during lay-up, and composite shrinkage during the manufacturing of large, thick and complex structural elements, are also concerns. During the HSR, a workable autoclave molding cycle was developed for manufacturing large IM7/PETI-5 composite

parts, which proved to be robust with high quality laminates such as face sheets for sandwich structures (1/4"- 3/8", 50 to 75 plies), skins for skin stringer structures (0.3" - 0.5", 60 to 100 plies), and wing box structures (1", 200 plies) as large as 1.8 m x 3.0 m [8, 9]. This paper addresses a few issues regarding the processing robustness of the IM7/PETAA-5/NMP composite prepreg. The cure cycle is optimized by means of the fractional factorial experimental design methodology.

## 2. EXPERIMENTAL<sup>†</sup>

### 2.1 Materials

LARC<sup>™</sup> PETI-5 is a phenylethynyl-terminated imide resin developed by NASA Langley Research Center (LARC) during the 1990s. The PETAA-5/NMP is made from the reaction of 3,3',4,4'-biphenyltetracarboxylic dianhydride, an 85:15 molar ratio of 3,4'-oxydianiline and 1,3-bis(3-aminophenoxy)benzene, and 4-phenylethynylphthalic anhydride (PEPA) as the endcapper, in solvent NMP at a theoretical number average molecular weight of ~5,000 g/mol [2-7]. Two batches of IM7/PETAA-5/NMP prepreg were used in this study. The sources and characteristics of these prepreps are summarized in Table 1. Unless otherwise stated, results discussed were obtained from prepreps made at NASA LARC.

Table 1. IM7/PETAA-5/NMP prepreps

Source	Lot	Width, in	FAW, g/m <sup>2</sup>	Volatile cont., % w/w	Resin cont., % w/w	Handlability
NASA LaRC	TM-103	10.5	135	15.5	39.1	moderately tacky and drapable
* ICI Fiberite	31740Q	24	143	22.9	36	very tacky and drapable

\* Now Cytec Fiberite, Tempe, Arizona

### 2.2 Viscoelastic Measurements

Rheological measurements were conducted on a Rheometrics System IV rheometer. Both neat resin and composite were characterized. Neat resin measurements were performed using parallel-plate geometry, while torsional rectangular geometry was employed for composite prepreg measurements. For neat resin measurement, sample specimen disks, 2.54 cm in diameter and ~ 1.5 mm thick, were prepared by press molding the thermally pre-treated PETI-5 powder at room temperature (RT). The compacted resin disk was then loaded between parallel plates in the rheometer. For composite measurement, four to six plies of IM7/PETAA-5/NMP prepreg measuring 2.5" x 0.5" were stacked and gripped on both ends by the rheometer fixture, affording an effective gauge length of approximately 1.5". Dynamic mode was used in both cases. During measurement, a controlled strain of 5% and angular frequency of 10 rad/sec were

<sup>†</sup>Use of trade names or manufacturers does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.  
maintained for specimen deformation. The resultant torque was recorded by a transducer. These torque values were decomposed into in-phase and out-of-phase components. Material properties such

as storage modulus ( $G'$ ), loss modulus ( $G''$ ) and complex viscosity ( $\eta^*$ ) were readily derived by the principle of linear viscoelasticity.

### 2.3 Acoustic Measurements

Ultrasonic C-scans were performed in pulse echo mode using a 5 MHz Parametrics transducer with 0.5" diameter and 4" focal distance, and a Parametrics 5055 pulse receiver. Gate was set over an auxiliary glass reflector. All measurements were performed at an attenuation value of 10 dB, step and index 0.040 in., pulse repetition rate 0.03 MHz, and receiver gain -20 dB.

### 2.4 Mechanical Measurements

Open hole compression (OHC) strength values using Northrop specification [9] were measured at RT (dry) and 177°C (wet). Wet specimens were prepared by immersing in water at RT. Periodically, weights were measured until stable values were reached. Laminate lay-up was  $[\pm 45/90/0/0/\pm 45/0/0/\pm 45/0]_2$ . Specimen dimensions were 1" x 3" with 0.25" diameter hole in the center.

### 3. RESULTS AND DISCUSSION

#### 3.1 Prepreg shelf life

Polymeric resin impregnated prepreg requires a long shelf life to withstand the severe fabrication environment where, over a period of time, trimming, laying, bagging and curing into structural parts occur. To evaluate the shelf life, IM7/PETAA-5/NMP wet prepregs were sealed in polyethylene bags and stored at ambient for 30 and 60 days, respectively.

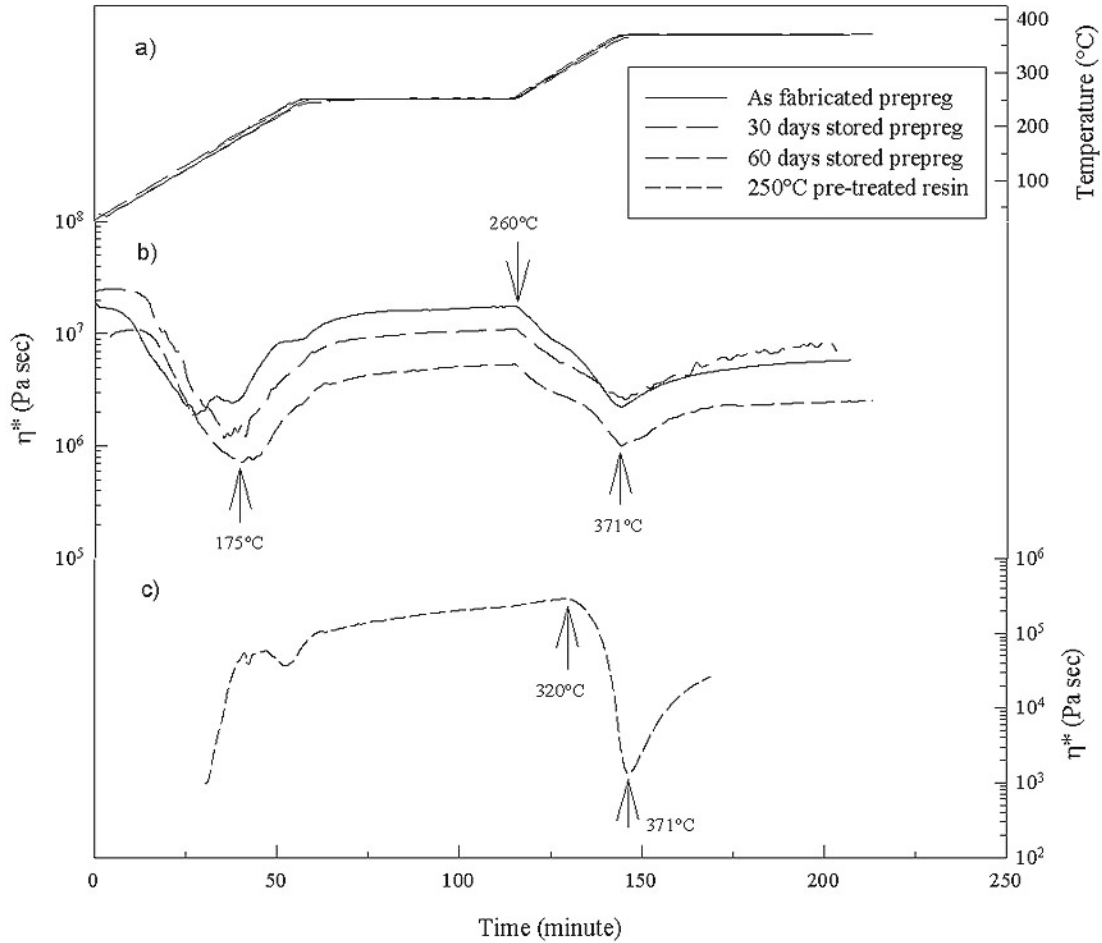


Figure 1. Rheological properties of PETAA-5/NMP resin and prepreg.

Figure 1 shows rheological measurements for the as-fabricated as well as the ambient-stored prepregs. The same temperature profile as shown in Figure 1a) was used for all measurements: a 4°C/min heating from RT to 250°C and hold for 1 hr, followed by a 4°C/min heating to 371°C and hold for 1 hr. Values of  $\eta^*$  as a function of time are presented in Figure 1b). Although variations in

the measured viscosity levels are observed, the transition characteristics are similar among these three measurements. The variations in  $\eta^*$  among the three measurements were partially attributed to the different number of prepreg plies used as evidenced by the initial values at the beginnings of measurements. Prepreg viscosity dropped initially as temperatures rose from RT due to the softening of the resin matrix. When temperatures exceeded approximately 175°C, solvent evaporation and initial imidization reactions led to a stiffer matrix with higher  $\eta^*$ . Viscosities were relatively stable during the 250°C/1 hr hold period. During the second temperature ramp, another significant drop in viscosity began at 260°C and ended at 371°C. Beyond the minimum viscosity at 371°C, the matrix resin gelled quickly, resulting in higher viscosities due to the crosslinking reactions.

Also included (Figure 1c)) is the viscosity curve for the PETAA-5/NMP neat resin measured under the identical temperature profile. PETAA-5/NMP resin was taken from wet prepreg flash and thermally pre-treated at 250°C/1 hr in an oven before measurement. An earlier study reported that less than 0.5% w/w volatiles remained after the 250°C/1 hr thermal pre-treatment [7]. Because of the presence of reinforcing fibers, prepreg viscosities (in Figure 1b)) were artificially inflated about two orders of magnitude when compared to the neat resin viscosity. Thermally pre-treated neat resin behaved quite differently from wet prepreg during the initial heat-up period. Critical transition characteristics were similar between these two materials, however. During the initial temperature ramp, the resin specimen softened and interfacial adhesive strength between the resin and the parallel-plate fixture increased, which led to an (artificial) increase in viscosity during this period. The observed slight increase in viscosity during the 250°C/1 hr hold in Figure 1c) was attributed to the imidization (chain extension) reactions of the residual PETI-5 oligomers. A significant drop in viscosity occurred at 320°C with a minimum viscosity reached at approximately 5 mins into the 371°C/1 hr hold period. The higher softening temperature measured for the neat resin (i.e., 320°C) versus the wet prepreg (i.e., 260°C) was again attributed to the difference of the specimens' thermal histories. The observed abrupt rise in viscosity from the minimum at elevated temperatures was due to the crosslinking reaction of the PEPA endgroups in the PETI-5 molecules.

From a processing point of view, these results suggest that IM7/PETAA-5/NMP wet prepreg rheology is not affected by the prolonged ambient storage. Transition temperatures for the matrix softening (260°C) and the occurrence of minimum viscosity (371°C) are identical among prepreps. Furthermore, the same amount of viscosity drop between 260° and 371°C in Figure 1b) was also noted, which suggests that the residual matrix fluidities after a 250°C/1 hr B-stage are very similar among the as-fabricated and the ambient stored prepreps.

OHC strengths for the laminates made from these ambient-stored prepreps are tabulated in Table 2. No statistically significant differences existed between the as-fabricated and the 60-days-stored specimens. Both were made from NASA LARC prepreps. Specimens made from ICI Fiberite commercial prepreps, however, consistently yielded higher OHC strength values, i.e., approximately

10 and 5% higher at RT and 177°C, respectively. These differences are attributed to the differences in prepreg quality.

Table 2. Effect of ambient storage for IM7/PETI prepregs

Source	Duration of ambient storage	*Residual volatiles (% w/w)	OHC strength, Ksi	
			RT	177°C (wet)
NASA LaRC	As-fabricated	18.5	59.9 ± 1.1	44.2 ± 1.5
ICI Fiberite	30 days	18	65.5 ± 1.0	46.3 ± 1.3
NASA LaRC	60 days	17	57.3 ± 2.3	43.1 ± 2.4

\* Residual volatiles were measured by TGA on resin flash from the aged prepregs. % w/w values were based on neat resin weight only.

### 3.2 Effect of B-stage conditions

The imidization reaction of PETAA-5/NMP oligomers releases water as reaction by-product. This water and NMP mixture needs to be thermally depleted prior to the pressure consolidation in order to prevent formation of voids inside the laminate during curing. The thermal treatment condition and duration (temperature and time) in the absence of pressure is called B-stage. Inclusion of B-stage in a cure cycle is often necessary to deplete volatiles. From a processing viewpoint, a reasonably wide B-stage window is desired for the prepreg materials in order to accommodate variations of processing conditions incurred during the fabrication of large composite structure parts in an autoclave. Lowering the B-stage temperature will likely retain excessive residual volatiles in the (wet) prepreg plies, resulting in voided parts. On the other hand, raising the B-stage temperature will potentially advance the PEPA endgroups' crosslinking reactions, resulting in decreased fluidity of the (curing) resin matrix, and compromising its processability under a moderate pressure. In an earlier weight loss study, results indicated that less than 0.2% residual volatiles remained in the PETAA-5/NMP prepreg after 1 hr at 250°C [7]. The B-stage window for this prepreg system is explored in this section.

Rheological measurements on neat resin under simulated autoclave cure cycles (temperature profiles) were conducted with 1 hour at 250°C, 1 hour at 300°C, and 0.5 hour at 350° respectively (see Figure 2). In order to prevent resin foaming during measurement, each specimen was thermally pre-treated 1 hr in an oven at its respective B-stage temperature. A subsequent 1 hr hold at 371°C which simulates the final composite consolidation step was used in all cases.

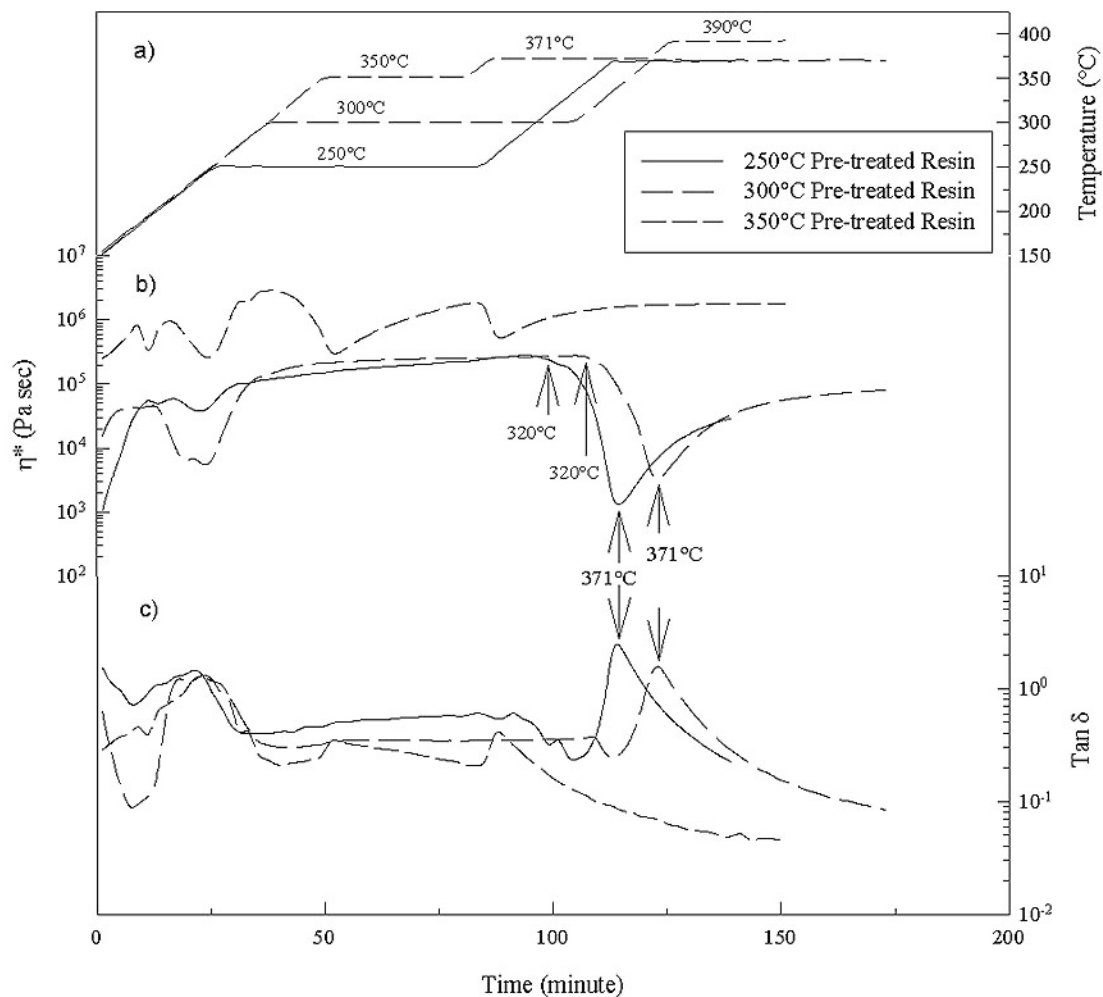


Figure 2. Rheological properties of B-staged PETAA-5/NMP resins.

Temperature profiles, measured  $\eta^*$  and  $\tan \delta$  for the three B-stage specimens are shown in Figures 2 a), b) and c), respectively. Variations of  $\eta^*$  and  $\tan \delta$  values during the initial ramp-and-hold period (i.e., from RT to the respective B-stage hold temperature) are artifacts for the same reason discussed in Section 3.1. When comparing the viscoelastic properties between the 250°C/1 hr and the 300°C/1 hr pre-treated specimens in the respective B-stage hold period, both values of  $\eta^*$  and  $\tan \delta$  were relatively stable, with slightly lower  $\eta^*$  and higher  $\tan \delta$  values measured for the 250°C/1 hr specimen. Higher  $\tan \delta$  values for the 250°C/1 hr B-stage specimen indicated an (expected) enhanced degree of viscoelastic solid-like behavior. During the second ramp to 371°C, a sharp drop in  $\eta^*$  values occurred at approximately 320°C for both specimens due to the melting of resin. Upon melting,  $\eta^*$  continued to decrease and a minimum was reached at approximately 5 mins into the 371°C hold. The

minimum values were measured at  $10^3$  Pa sec and  $3 \times 10^3$  Pa sec, respectively, for the 250°C/1 hr and 300°C/1 hr B-stage specimens. The higher minimum viscosity exhibited by the 300°C/1 hr B-stage specimen indicated that its processability had been slightly compromised due to the more severe B-stage condition employed. Subsequent increases in viscosities were due to the crosslinking reactions of the reactive PEPA endgroups at elevated temperatures. These reactions were also manifested by the formation of a gelation point at  $\tan \delta = 1$ . At the gel point the specimens were quickly transformed to become viscoelastic solid-like, as evidenced by a rapid decrease in  $\tan \delta$  and increase in viscosity values.

Rheological measurements for the 350°C/1 hr B-stage specimen are also included in Figures 2b) and c). Very different  $\eta^*$  (t) and  $\tan \delta$  (t) behavior were observed. The specimen appeared to be solid-like during the entire measurement with insufficient resin-metal interfacial adhesion. Severe interfacial stick-and-slip motions between specimen and parallel-plate fixture were evident. The minimum viscosity in the  $10^3$  Pa sec order of magnitude and the gelation point in which  $\tan \delta = 1$  were absent. These results suggest that the 350°C/1 hr B-stage condition is too severe for the PETAA-5/NMP wet prepreg. After the 350°C/1 hr thermal pre-treatment, the crosslinking reaction was advanced along with volatile depletion, resulting in a severe loss of processability. In fact, values of  $\eta^*$  did not decrease during a temperature ramp from 371°C to 390°C (see Figure 2b)), suggesting that the crosslink reactions were completed in the 370°C/0.5 hr hold period.

From these results, one concludes that the residual processability of PETI-5 matrix resin is indifferent when subjected to a broad B-stage window from 250°C/1 hr to 300°C/1 hr. B-staged resin matrix softens at 320°C and exhibits a minimum viscosity at 371°C. At 5 to 10 minutes into the 371°C hold, the resin gels and viscosity increases abruptly with a fast diminishing processability due to crosslinking reactions. It becomes apparent that the consolidation pressure must be applied shortly after the B-stage period in order to exploit maximum residual fluidity between 320° and 371°C to achieve complete resin impregnation within the laminate.

Measured OHC strengths are tabulated in Table 3 for laminates consolidated at the various B-stage conditions discussed above. A final 371°C/1 hr cure with 200 Psi was used in all cases. When taking into account the standard deviations, both RT and 177°C OHC strength values were indistinguishable among specimens. Average strength values were 56.5 Ksi at RT (dry) and 42.0 Ksi at 177°C (wet). These results appear to confirm the rheological studies discussed above. They also suggest that PETI-5 matrix resin's volatile depletion rate is more sensitive to the B-stage temperature than the B-stage duration, as evidenced by the result of Specimen No. 5 in Table 3.

Table 3. Effect of B-stage conditions on the OHC strength values

Spec. ID	B-stage condition	Consolidation	OHC Strength, Ksi
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		Temperature	Pressure (Psi)	RT (dry)	177°C (wet)
1	250°C/0.5 hr	371°C/1.0 hr	200	57.8 ± 2.8	39.7 ± 3.7
2	250°C/1.0 hr	371°C/1.0 hr	200	59.9 ± 3.0	44.2 ± 1.2
3	300°C/0.5 hr	371°C/1.0 hr	200	55.0 ± 0.7	44.3 ± 3.3
4	300°C/1.0 hr	371°C/1.0 hr	200	54.5 ± 2.0	42.1 ± 0.2
5*	No Hold	371°C/1.0 hr	200	55.4 ± 2.3	39.6 ± 1.8

\* In this case, pressure was applied at 300°C during the temperature ramp. In other cases, pressure was applied at the end of B-stage period.

^ 1 Psi = 6.897 KPa.

### 3.3 Composite OHC strength

OHC specimens of the PETI-5 composites were fabricated in a vacuum press using the following cure cycle:

1. Temperature was ramped from RT to 250°C and held for 1 hr (i.e., B stage). In this period, full vacuum was drawn, but with no pressure applied to the prepreg plies.
2. Temperature was ramped from 250°C to the curing temperature, CT, and held for 1 hr. In this period, full vacuum was continued and a consolidation pressure, CP, was applied at the beginning of the ramp.
3. Cooling down. Vacuum and pressure were relieved when temperature reached 150°C.

OHC strength of composites fabricated from two different prepreg sources are compared in Table 4. Each OHC strength reported in the table represented a mean value averaged from three specimens. The standard deviations were similar to those reported in Table 3 above. It was noted that laminates fabricated from the Cytec Fiberite prepreps yielded higher OHC strengths at lower CPs. For example, composites made from Cytec Fiberite prepreps at 370°C using 100 Psi exhibited a strength level which was unmatched by those laminates made from NASA LaRC prepreps using higher CPs. This is attributed to the differences in prepreg quality. Among the OHC strengths of NASA LaRC composites at the maximum allowable CT (i.e., 370°C), both RT (dry) and 177°C (wet) values were similar, irrespective of the employed CP levels. On the other hand, at the maximum allowable consolidation pressure, CP = 200 Psi, 5% and 15% drops, respectively for the RT (dry) and 177°C (wet) OHC strengths were observed for CT = 355°C. Similarly, for composites made from the (higher quality) Cytec Fiberite prepreps, significantly lower strength values were measured at CT = 340°C and CP = 200 Psi. These results strongly suggest that CT is a more sensitive molding parameter than CP in the fabrication of IM7/PETI-5 composites.

Table 4. Comparison of the OHC strengths from different prepreg sources

CT, °C	CP, Psi	OHC Strength, Ksi			
		NASA LaRC prepreg		Cytec Fiberite prepreg	
		RT (dry)	177°C (wet)	RT (dry)	177°C (wet)
370	200	59	44	---	---
	175	55	44	---	---
	160	56	48	---	---
	100	---	---	62	44
360	185	55	43	---	---
355	200	53	37	---	---
350		---	---	58	37
340		---	---	45	32
355	175	54	33	---	---
350	150	---	---	57	34
350		52	35	---	---

### 3.4 Determination of critical curing parameters

A cure cycle consisting of a two-step temperature profile is shown in Figure 3. Curing variables such as heating rate, B-stage temperature and duration, consolidation temperature and duration,

pressure level and pressure application point (PAP), and their functionalities during composite fabrication are summarized in Table 5.

For the IM7/LARC™ PETI-5 composite fabrication, the molding conditions are restricted to 200 Psi and 371°C (700°F) because of the restricted pressure and temperature associated with large commercial autoclaves. Molding variable No. 1 (i.e., heating rate in Table 5) is essentially fixed at 1 to 4°C/min for the same reason. Based on the rheological studies in Section 3.2 above, it is reasonable to keep the prepreg B-stage conditions (variables No. 2 and 3 in Table 5, i.e., temperature and duration) unchanged at 250°C/1 hr for this prepreg system.

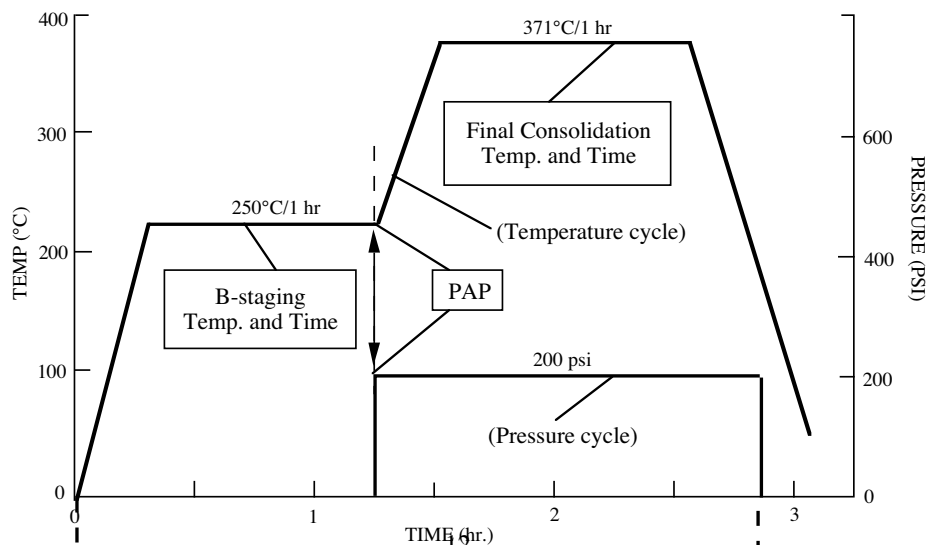


Figure 3. A cure cycle consisting two-step temperature, one-step pressure and vacuum profiles.

Table 5. Critical molding variables and functionalities for composite fabrication

Molding Variable		Functionalities
1	Heating rate	<ul style="list-style-type: none"> <li>• A higher heating rate leads to a shorter molding cycle and a more economical fabrication process. However, the processing window may be narrowed for a reactive resin matrix. This is particularly true during the second ramp to 371°C.</li> </ul>
2	B-stage temperature	<ul style="list-style-type: none"> <li>• A necessary step for volatile depletion before commencing consolidation.</li> <li>• The selected temperature should be high enough for imidization reaction, but low enough to avoid pre-mature advancement of the endgroups' crosslinking reaction.</li> </ul>
3	B-stage duration	<ul style="list-style-type: none"> <li>• The selected duration time should be long enough to adequately deplete volatiles.</li> </ul>
4	Consolidation temperature	<ul style="list-style-type: none"> <li>• The selected temperature must fully exploit the residual fluidity afforded by the B-stage reactive resin matrix, while at the same time, conforming to the capacity of the molding equipment.</li> <li>• For the PETI-5 matrix, this temperature must be higher than <math>T_m</math> (~350°C) of crystallinity generated during 250°C/1 hr B-stage period [7].</li> </ul>
5	Duration of consolidation	<ul style="list-style-type: none"> <li>• The selected duration time should be long enough to achieve full consolidation of the laminate.</li> </ul>
6	Consolidation pressure	<ul style="list-style-type: none"> <li>• The selected pressure should be adequate for resin impregnation within the consolidating laminate without causing excessive resin loss.</li> </ul>
7	Pressure application point (PAP)	<ul style="list-style-type: none"> <li>• In order to fabricate void-free, well-consolidated laminate, the PAP should be selected based upon a balance between two opposing factors: the residual volatile contents in the prepreg and the remaining fluidity of the matrix resin. Achieving such a balance could be challenging when dealing with reactive resin systems [7].</li> </ul>

Furthermore, based on an earlier study which showed that residual volatiles in the prepreps are less than 0.2% w/w at the end of 250°C/1 hr B-stage [7], the PAP (variable No. 7 in Table 5) can safely be selected to be the end of the B-stage period. Pressure is held thereafter to achieve complete resin impregnation within the laminate, fully exploiting the residual matrix fluidity. A consolidation period

(variable No. 5 in Table 5) of 371°C for 1 hr is required to afford the complete curing of PETI-5 chemistry. Therefore, there are only two variables remaining, i.e., the curing temperature (CT) and the consolidation pressure (CP), which will be optimized in the molding cycle design for the IM7/PETAA-5/NMP prepreg system.

### 3.5 Experimental Design

Fractional factorial design was used here to explore the optimal molding window for the IM7/PETAA-5/NMP composite. The CT and CP were considered as two independent processing variables. The ultrasonic C-scan image of the consolidated laminate was used as a measure of laminate consolidation quality. This problem was tackled from the standpoint of response surface methodology [10, 11]. Ultrasonic C-scan images were used to estimate laminate consolidation quality. A regression analysis was used to estimate laminate quality at a given CT and CP, and also to identify optimal combinations of CT and CP in the molding cycle which would likely produce the maximum quality of consolidation.

Table 6. Box-Wilson Central Composite Design

Run	CT <sub>coded</sub>	CP <sub>coded</sub>	CT (°C)	CP (Psi)	CSQ (%)*
1	-1	-1	332	115	0.05
2	1	-1	364	115	5.05
3	-1	1	332	185	35.54
4	1	1	364	185	96.26
5	-1.414	0	325	150	0.07
6	1.414	0	371	150	83.8
7	0	-1.414	348	100	2.1
8	0	1.414	348	200	81.22
9	0	0	348	150	50.44
10	0	0	348	150	53.93
11	0	0	348	150	45.46
12	0	0	348	150	71.04
13	0	0	348	150	55.05

\* C-Scan Quality

The thirteen experiments shown in Table 6 with coded molding variables are organized according to the Box-Wilson Central Composite (BWCC) design. Regions of interest for the two processing variables were selected as  $325^{\circ}\text{C} < \text{CT} < 371^{\circ}\text{C}$  and  $100 \text{ Psi} < \text{CP} < 200 \text{ Psi}$ . The scaling factors were  $\text{CT}_{\text{scaling factor}} = 16.26^{\circ}\text{C}$  and  $\text{CP}_{\text{scaling factor}} = 35.36 \text{ Psi}$ . Values of CT and CP for each experiment obtained by the following formula are included in Table 6:

$$\text{CT} = \text{CT}_{\text{coded}} \times \text{CT}_{\text{scaling factor}} + 348$$

$$\text{CP} = \text{CP}_{\text{coded}} \times \text{CP}_{\text{scaling factor}} + 150$$

A unidirectional 3" x 3" – [0]<sub>24</sub> composite panel was fabricated at each experimental condition. The percentage of the area on each panel exhibiting greater than the 90% threshold consolidation, as measured by digitized C-scan images, is also included in Table 6. Area percentage so derived is denoted as C-Scan Quality (CSQ) for a given panel. The 90% threshold cut-off was chosen based on the experimentally established correlation between the C-scan image and the unidirectional

composite consolidation quality. C-scans were measured using identical pre-determined conditions for all panels.

### 3.6 Regression Analysis

Results in Table 5 were used to construct the following non-linear regression equation:

$$CSQ = b_0 + b_1 CT + b_2 CP + b_{11} (CT)^2 + b_{22} (CP)^2 + b_{12} (CT)(CP) \quad (1)$$

where CSQ denotes C-Scan Quality of the panels in percent. The procedure for analysis and the values of coefficients of Eq. (1) are tabulated in Table 7.

The significance of each term in the regression equation was examined by the standard error and the *t* test. An estimate of variance, *S* = 9.62, was also obtained. These values are included in Table 7. A

significance with at least a 95% confidence level for each regression coefficient is obtained. The final regression equation is represented by Eq. (2) below:

$$CSQ = 55.18 + 23.01 CT + 29.82 CP - 8.52 (CT)^2 - 8.66 (CP)^2 + 13.93 (CT)(CP) \quad (2)$$

Table 7. Regression Analysis for the Box-Wilson Central Composite Design

Expt. Run	C-Scan Quality (%)	CT	CP	(CT) <sup>2</sup>	(CP) <sup>2</sup>	(CP)x(CT)
1	.05	-0.05	-0.05	0.05	0.05	0.05
2	5.05	5.05	-5.05	5.05	5.05	-5.05
3	35.54	-35.54	35.54	35.54	35.54	-35.54
4	96.26	96.26	96.26	96.26	96.26	96.26
5	.07	-0.10	0	.14	0	0
6	83.80	118.49	0	167.60	0	0
7	2.10	0	-2.97	0	4.20	0
8	81.22	0	114.85	0	162.44	0
9	50.44	0	0	0	0	0
10	53.93	0	0	0	0	0
11	45.46	0	0	0	0	0
12	71.04	0	0	0	0	0

13	55.05	0	0	0	0	0
Total	580.01	184.11	238.58	304.64	303.54	55.72

Regression Parameters	$b_0$	$b_1$	$b_2$	$b_{11}$	$b_{22}$	$b_{12}$
	55.18	23.01	29.82	-8.52	-8.66	13.93
Strd. error	3.41	3.41	3.41	3.65	3.65	4.81
$t$ test	16.18	6.75	8.75	2.33	2.37	2.90
% confidence	99+	99+	99+	95+	95+	97.5+

### 3.7 Optimal Molding Condition

A CSQ contour surface mapping, based on CT and CP molding variables, generated from Eq. (2) is shown in Figure 4. The CSQ value is labeled for each contour curve. It is apparent from the figure that higher CT and CP processing conditions would yield laminates with higher percentage values of CSQ. A processing window can be defined as bordered by a set of CT, CP and CSQ contour curve. The processing window which would yield laminates with 100% CSQ is predicted to be the region bounded by CP = 200 Psi, CT = 370°C and the 100% CSQ contour curve. The regression model also suggests that the percentage CSQ decreases with lower CT and CP conditions. This is consistent with the experimental observations. It was reported that double crystalline melting peaks at 290°C and 353°C were induced in the PETI-5 resin matrix when subjected to 250°C/1 hr annealing [7]. When CT is lower than these crystalline melting temperatures, residual fluidity is reduced and composite processability is likely to suffer under such a situation.

Also included in Figure 4 are discrete RT (dry) and 177°C (wet) OHC strength values measured at several molding conditions as tabulated in Table 4. Composite strength values are from NASA LaRC prepreg only for the reasons discussed in Section 3.3 above. These measured strength values exhibited a similar trend as that illustrated by the CSQ contour curves in the figure. Slightly enhanced OHC strengths were noted toward higher CT and CP conditions among laminates with better than 80% CSQ. When comparing laminates fabricated at CP = 200 Psi, the OHC strengths deteriorated rapidly when CT was lower than 355°C. On the other hand, the OHC strengths were lowered only slightly with decreasing CP when comparing laminates fabricated at CT  $\geq$  350°C. CT is therefore a more sensitive molding parameter than CP in the fabrication of the IM7/PETI-5 composite. The regression model correctly predicted such a trend, particularly in the regions where CTs are below 350°C. As CTs increased, such a sensitivity diminished as observed from the experimental OHC strength values (i.e., in the regions where CSQ > 80% and CT > 360°C) included in the figure.

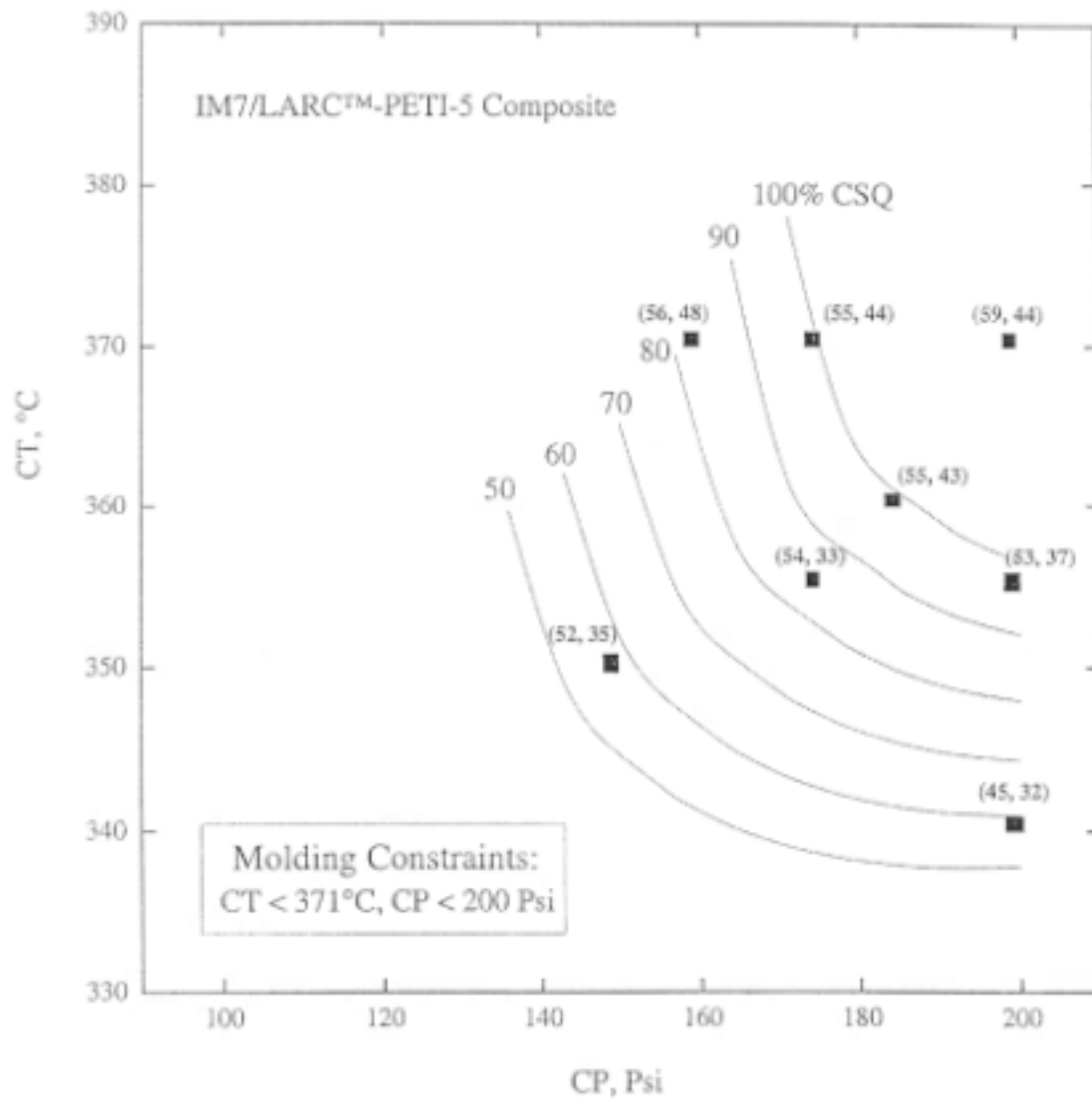


Figure 4. Response surface mapping constructed by the regression model. The first and the second values in parenthesis represent the RT (dry) and the 177°C (wet) OHC strengths, respectively, at each discrete molding condition.

#### 4. CONCLUSIONS

Processing robustness of IM7/PETI-5 was investigated with respect to the prepreg shelf life, the effect of B-stage conditions, and the optimal processing window. Rheological measurements were found to be useful in the processability evaluation of the ambient stored prepregs. Prepreg rheology was not affected by prolonged (i.e., up to 60 days) ambient storage. Critical prepreg characteristics such as the initial softening temperature of the matrix resin (i.e.,  $\sim 260^{\circ}\text{C}$ ), minimum viscosity, and the temperature of minimum viscosity (i.e.,  $371^{\circ}\text{C}$ ) were all retained by the aged prepregs. Both RT and  $177^{\circ}\text{C}$  (wet) OHC strength values of laminates were found to be unaffected as well.

Rheological measurements suggest that the processability of PETI-5 matrix resin is only slightly affected over a wide range of B-stage temperatures from  $250^{\circ}$  to  $300^{\circ}\text{C}$ . Both RT and  $177^{\circ}\text{C}$  (wet) OHC strength values are statistically indistinguishable among composite specimens B-staged at  $250^{\circ}\text{C}/0.5$  hr,  $250^{\circ}\text{C}/1$  hr,  $300^{\circ}\text{C}/0.5$  hr or  $300^{\circ}\text{C}/1$  hr, respectively, and consolidated at  $371^{\circ}\text{C}$  for 1 hr. Such a wide B-stage window allows IM7/PETI-5 prepreg to accommodate the processing variations associated with different sizes of fabrication equipment and composite parts.

The Box-Wilson Central Composite design was used to optimize molding conditions for IM7/PETI-5 composites. The regression model suggests that the percentage CSQ increases with higher CT and CP conditions, consistent with the experimental observations. The processing window which would yield laminates with 100% CSQ is predicted to be the region bounded by  $\text{CP} = 200$  Psi,  $\text{CT} = 370^{\circ}\text{C}$  and the 100% CSQ contour curve. It was found that the response surface methodology is a useful tool in process optimization. The IM7/PETI-5 composite was found to be more sensitive to the consolidation temperature than to the consolidation pressure. At maximum allowable temperature (i.e.,  $371^{\circ}\text{C}$ ), good laminate quality was achievable at 100 Psi. However, the processability dropped dramatically at consolidation temperatures below  $350^{\circ}\text{C}$ . At  $340^{\circ}\text{C}/200$  Psi, for example, the RT OHC strength was reduced from a nominal 56 Ksi to 45 Ksi. This was attributed to the reduced fluidity associated with the semi-crystalline matrix, that was generated during the  $250^{\circ}\text{C}/1$  hr B-stage used throughout this investigation.

The processability of the IM7/ LARC<sup>TM</sup> PETI-5 prepreg was found to be robust. The resin matrix's residual fluidity is unaffected by the B-stage conditions over a wide range of temperatures. Subjected to the constraints of commercial autoclave, the optimal molding conditions were found to be bounded by  $\text{CT} \leq 370^{\circ}\text{C}$ ,  $\text{CP} \leq 200$  Psi, and a 85% CSQ response surface contour curve derived from a regression analysis.

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