

Processing Robustness for a Phenylethynyl-Terminated Polyimide Composite

T. H. Hou

Langley Research Center, National Aeronautics and Space Administration, Hampton, Virginia 23681-0001

Received 20 April 2004; accepted 30 September 2004

DOI 10.1002/app.21625

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The processability of a phenylethynyl-terminated imide resin matrix (PETI-5) composite was investigated. Unidirectional prepregs were made through the coating of an *N*-methylpyrrolidone solution of an amide acid oligomer (PETAA-5/NMP) onto unsized IM7 fibers. Two batches of prepregs were used: one was made by the National Aeronautics and Space Administration in house, and the other was from an industrial source. The composite processing robustness was investigated with respect to the prepreg shelf life, the effect of B-staging conditions, and the optimal processing window. The prepreg rheology and open hole compression (OHC) strengths were not affected by prolonged ambient storage (i.e., up to 60 days). Rheological measurements indicated that the PETAA-5/NMP processability was only slightly affected over a wide range of B-stage temperatures (from 250 to 300°C). The OHC strength

values were statistically indistinguishable among laminates consolidated under various B-staging conditions. An optimal processing window was established with response surface methodology. The IM7/PETAA-5/NMP prepreg was more sensitive to the consolidation temperature than to the pressure. A good consolidation was achievable at 371°C (700°F)/100 psi, which yielded a room-temperature OHC strength of 62 ksi. However, the processability declined dramatically at temperatures below 350°C (662°F), as evidenced by the OHC strength values. The processability of the IM7/PETI-5 prepreg was robust. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3212–3221, 2006

Key words: composites; curing of polymers; polyimides; voids

INTRODUCTION

In 1989, the National Aeronautics and Space Administration (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 temperature 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 h. In addition to this long-term durability requirement, the candidate matrix resin and composite had to exhibit no toxicity, high mechanical properties from –54 to 177°C, resistance to moisture and solvents, no microcracking under thermal cycling, acceptable handleability, robust processability under less than 1.4 MPa (200 psi) of pressure and at less than 370°C (700°F), and amenability to different fabrication processes, such as automated tape placement and auto-

clave curing. A phenylethynyl-terminated imide resin matrix (PETI-5) was selected as the candidate material for scale-up in the HSCT airframe application. PETI-5 is an imide oligomer terminated with phenylethynyl groups. It has an attractive combination of properties demanded by the HSCT both as an adhesive and as a composite matrix.^{1–7}

PETI-5 has been primarily synthesized as an oligomeric (amide acid) solution in *N*-methylpyrrolidone (NMP) and is designated here as PETAA-5/NMP. Like many polyimides, the PETAA-5/NMP system releases a reaction byproduct (water) during imidization. A unidirectional IM7/PETAA-5/NMP wet prepreg contains about 22% (w/w) volatiles (the NMP solvent and the reaction byproduct water). It is well documented that volatile management in polyimide composite fabrication is a critical and challenging issue. To achieve void-free quality laminates, volatiles have to be depleted before the consolidation pressure (CP) is applied. 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 HSR, a molding cycle that included a 250°C/1-h B-stage and a 371°C/1-h stage with 200 psi consolidation was successfully designed for the IM7/PETAA-5/NMP prepreg system. Void-free laminates

The use of trade names or manufacturers does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

Correspondence to: T. H. Hou.

Journal of Applied Polymer Science, Vol. 100, 3212–3221, (2006)
Published 2006 Wiley Periodicals, Inc. *This article is a US Government work and, as such, is in the public domain in the United States of America.

TABLE I
IM7/PETAA-5/NMP Prepregs

Source	Lot	Width (in.)	FAW (g/m ²)	Volatile content (% w/w)	Resin content (% w/w)	Handleability
NASA LARC	TM-103	10.5	135	15.5	39.1	Moderately tacky and drapable
ICI Fiberite ^a	31740Q	24	143	22.9	36	Very tacky and drapable

^a Now Cytec Fiberite, Tempe, AZ.

^b FAW, fiber area weight.

with sizes up to 12" × 12" and 24 plies were fabricated with very good mechanical properties.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-h 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 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" and 50–75 plies), skins for skin-stringer structures (0.3–0.5" and 60–100 plies), and wing-box structures (1", 200 plies) as large as 1.8 m × 3.0 m.^{8,9} This article addresses a few issues regarding the processing robustness of the IM7/PETAA-5/NMP composite prepreg. The cure cycle was optimized with the fractional factorial experimental design methodology.

EXPERIMENTAL

Materials

PETI-5 was developed at the NASA Langley Research Center (LARC) during the 1990s. PETAA-5/NMP was 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 end capper in the solvent NMP at a theoretical number-average molecular weight of approximately 5000 g/mol.^{2–7} Two batches of the IM7/PETAA-5/NMP prepreg were used in this study. The sources and characteristics of these prepregs are summarized in Table I. Unless otherwise stated, the results were obtained from prepregs made at NASA LARC.

Viscoelastic measurements

Rheological measurements were conducted on a Rheometrics System IV rheometer (TA Instruments, New Castle, DE). Both the neat resin and composite were characterized. The neat resin measurements were performed with parallel-plate geometry, whereas torsional rectangular geometry was employed for the composite prepreg measurements.

For the neat resin measurements, sample specimen disks, 2.54 cm in diameter and approximately 1.5 mm thick, were prepared by the press molding of thermally pretreated PETI-5 powder at room temperature (RT). The compacted resin disk was then loaded between parallel plates in the rheometer. For the composite measurements, four to six plies of the IM7/PETAA-5/NMP prepreg, measuring 2.5" × 0.5", were stacked and gripped on both ends by the rheometer fixture, and this afforded an effective gauge length of approximately 1.5". The dynamic mode was used in both cases. During the measurements, a controlled strain of 5% and an angular frequency of 10 rad/s were 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 the storage modulus, loss modulus, and complex viscosity (η^*) were readily derived by the principle of linear viscoelasticity.

Acoustic measurements

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

Mechanical measurements

Open hole compression (OHC) strength values with the Northrop specification⁹ were measured at RT (dry) and 177°C (wet). Wet specimens were prepared by immersion in water at RT. Periodically, the weights were measured until stable values were reached. The

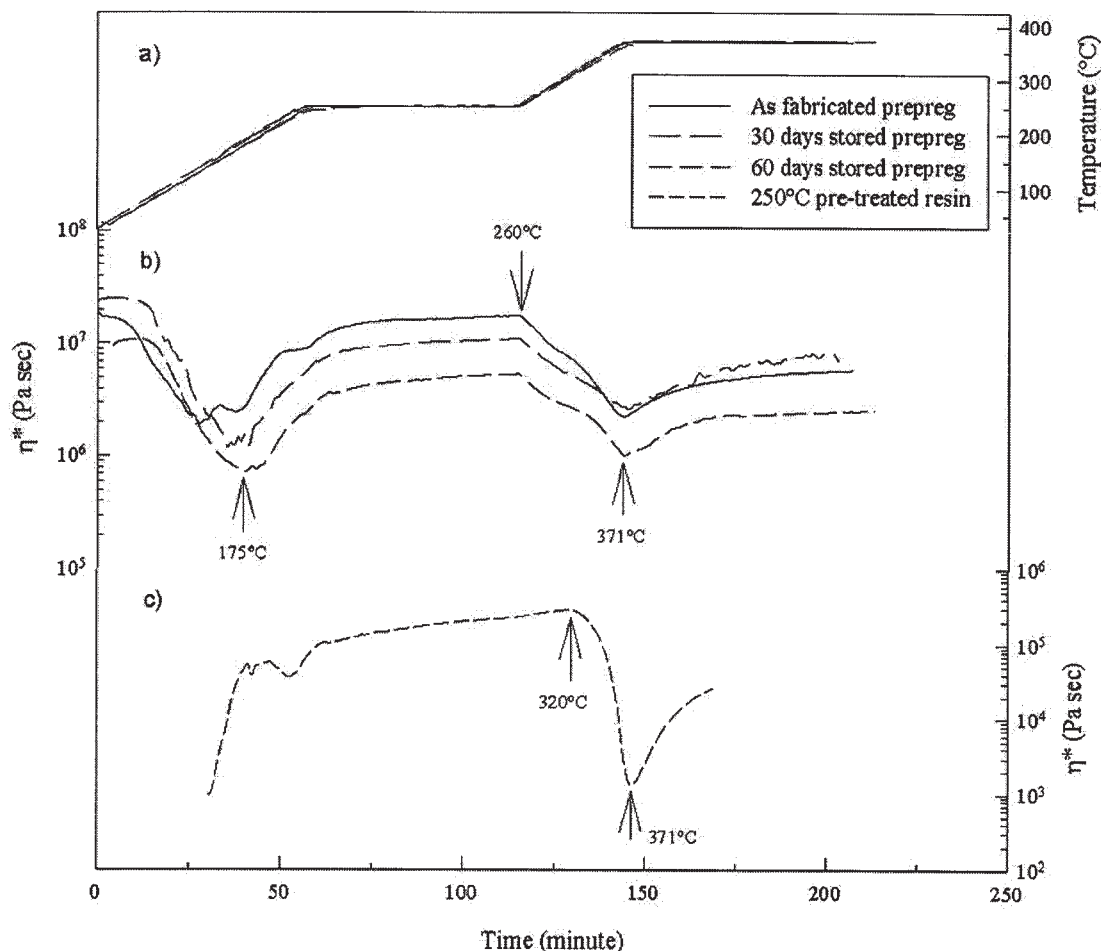


Figure 1 Rheological properties of the PETAA-5/NMP resin and prepreg.

laminates lay-up was $[\pm 45/90/0/0/\pm 45/0/0/\pm 45/0]_{2s}$. The specimen dimensions were $1'' \times 3''$, with a 0.25''-diameter hole in the center.

RESULTS AND DISCUSSION

Prepreg shelf life

A polymeric resin-impregnated prepreg requires a long shelf life to withstand a severe fabrication environment in which, over a period of time, trimming, laying, bagging, and curing into structural parts occur. For the evaluation of the shelf life, IM7/PETAA-5/NMP wet prepreps were sealed in polyethylene bags and stored under ambient conditions for 30 and 60 days, respectively.

Figure 1 shows rheological measurements for the as-fabricated and ambient-stored prepreps. The same temperature profile shown in Figure 1(a) was used for all the measurements: the prepreps were heated at $4^\circ\text{C}/\text{min}$ from RT to 250°C , held there for 1 h, heated at $4^\circ\text{C}/\text{min}$ to 371°C , and held there for 1 h. Values of η^* as a function of time are presented in Figure 1(b). Although variations in the measured viscosity levels

can be observed, the transition characteristics are similar among these three measurements. The variations in η^* among the three measurements can be partially attributed to the different numbers of prepreg plies used, as evidenced by the initial values at the beginnings of the measurements. The prepreg viscosity dropped initially as the temperatures rose from RT because of the softening of the resin matrix. When temperatures exceeded approximately 175°C , solvent evaporation and initial imidization reactions led to a stiffer matrix with a higher value of η^* . The viscosities were relatively stable during the $250^\circ\text{C}/1\text{-h}$ hold period. During the second temperature ramp, another significant drop in the viscosity began at 260°C and ended at 371°C . Beyond the minimum viscosity at 371°C , the matrix resin gelled quickly, and this resulted in higher viscosities because of the crosslinking reactions.

Also included [Fig. 1(c)] is the viscosity curve for the PETAA-5/NMP neat resin measured under an identical temperature profile. The PETAA-5/NMP resin was taken from a wet prepreg flash and was thermally pretreated at 250°C for 1 h in an oven before the

TABLE II
Effect of Ambient Storage for IM7/PETI Prepregs

Source	Duration of ambient storage	Residual volatiles (% w/w) ^a	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

^a Residual volatiles were measured by thermogravimetric analysis on resin flash from the aged prepregs. Weight-to-weight percentage values were based on neat resin weight only.

measurements. An earlier study reported that less than 0.5% (w/w) volatiles remained after the 250°C/1-h thermal pretreatment.⁷ Because of the presence of reinforcing fibers, the prepreg viscosities [Fig. 1(b)] were artificially inflated by about two orders of magnitude in comparison with the neat resin viscosity. The thermally pretreated neat resin behaved quite differently than the wet prepreg during the initial heating period. The critical transition characteristics were similar for these two materials, however. During the initial temperature ramp, the resin specimen softened, and the interfacial adhesive strength between the resin and the parallel-plate fixture increased; this led to an (artificial) increase in the viscosity during this period. The observed slight increase in the viscosity during the 250°C/1-h hold in Figure 1(c) was attributed to the imidization (chain-extension) reactions of the residual PETI-5 oligomers. A significant drop in the viscosity occurred at 320°C, with a minimum viscosity reached after approximately 5 min in the 371°C/1-h 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 differences in the specimens' thermal histories. The observed abrupt rise in the viscosity from the minimum at elevated temperatures was due to the crosslinking reaction of the PEPA end groups in the PETI-5 molecules.

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

The OHC strengths for the laminates made from these ambient-stored prepregs are listed in Table II. No statistically significant differences existed between the as-fabricated and 60-day-stored specimens. Both were made from NASA LARC prepregs. Specimens made from ICI Fiberite commercial prepregs, how-

ever, consistently yielded higher OHC strength values, that is, approximately 10 and 5% higher at RT and 177°C, respectively. These differences could be attributed to the differences in the prepreg quality.

Effect of the B-stage conditions

The imidization reaction of the PETAA-5/NMP oligomers releases water as a reaction byproduct. This water/NMP mixture needs to be thermally depleted before the pressure consolidation to prevent the formation of voids inside the laminate during curing. The thermal treatment conditions and duration (temperature and time) in the absence of pressure is called the B-stage. The inclusion of a 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 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, and this will result in voided parts. On the other hand, raising the B-stage temperature will potentially advance the PEPA end groups' 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, the results indicated that less than 0.2% residual volatiles remained in the PETAA-5/NMP prepreg after 1 h at 250°C.⁷ The B-stage window for this prepreg system is explored in this section.

Rheological measurements on the neat resin under simulated autoclave cure cycles (temperature profiles) were conducted for 1 h at 250°C, for 1 h at 300°C, and for 0.5 h at 350° (see Fig. 2). To prevent resin foaming during the measurements, each specimen was thermally pretreated for 1 h in an oven at its respective B-stage temperature. A subsequent 1-h hold at 371°C, which simulated the final composite consolidation step, was used in all cases.

Temperature profiles and measured η^* and $\tan \delta$ values for the three B-stage specimens are shown in Figure 2(a–c), respectively. The variations of η^* and

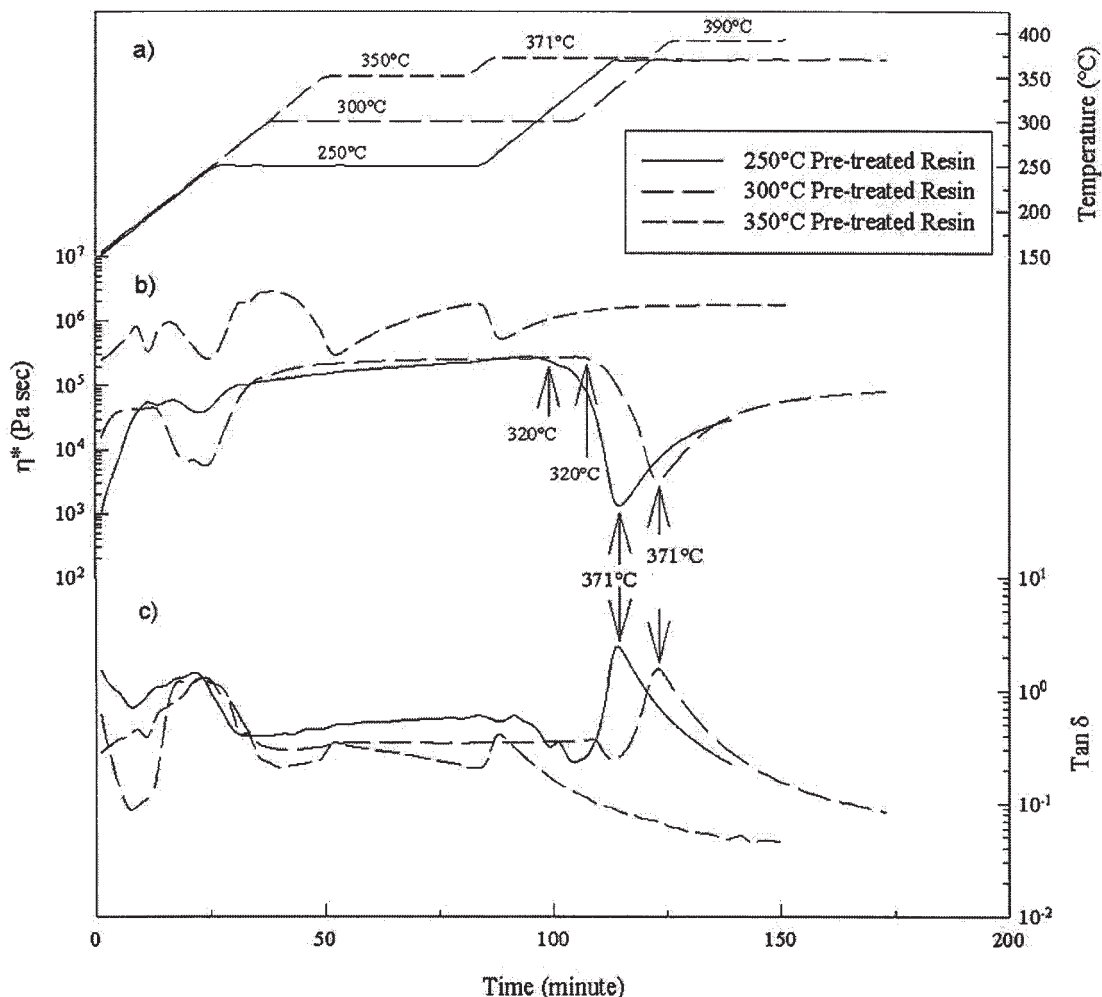


Figure 2 Rheological properties of the B-staged PETAA-5/NMP resins.

$\tan \delta$ during the initial ramp-and-hold period (i.e., from RT to the respective B-stage hold temperature) were artifacts for the same reason discussed earlier. In a comparison of the viscoelastic properties of the 250°C/1-h and 300°C/1-h pretreated specimens in the respective B-stage hold period, both η^* and $\tan \delta$ were relatively stable, with slightly lower η^* values and higher $\tan \delta$ values measured for the 250°C/1-h specimen. Higher $\tan \delta$ values for the 250°C/1-h B-stage specimen indicated an (expected) enhanced degree of viscoelastic, solid-like behavior. During the second ramp to 371°C, a sharp drop in η^* occurred at approximately 320°C for both specimens because of the melting of the resin. Upon melting, η^* continued to decrease, and a minimum was reached after approximately 5 min in the 371°C hold. The minimum values were measured at 10^3 Pa s and 3×10^3 Pa s, respectively, for the 250°C/1-h and 300°C/1-h B-stage specimens. The higher minimum viscosity exhibited by the 300°C/1-h B-stage specimen indicated that its processability had been slightly compromised by the more severe B-stage condition employed. Subsequent in-

creases in the viscosities were due to the crosslinking reactions of the reactive PEPA end groups 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, becoming viscoelastic and solid-like, as evidenced by a rapid decrease in $\tan \delta$ and an increase in the viscosity.

The rheological measurements for the 350°C/1-h B-stage specimen are also included in Figure 2(b,c). Very different $\eta^*(t)$ and $\tan \delta(t)$ behavior was observed. The specimen appeared to be solid-like during the measurements, with insufficient resin-metal interfacial adhesion. Severe interfacial stick-and-slip motions between the specimen and parallel-plate fixture were evident. The minimum viscosity with a 10^3 Pa s order of magnitude and the gelation point at which $\tan \delta$ was 1 were absent. These results suggest that the 350°C/1-h B-stage condition was too severe for the PETAA-5/NMP wet prepreg. After the 350°C/1-h thermal pretreatment, the crosslinking reaction was advanced along with volatile depletion, and this re-

TABLE III
Effect of B-Stage Conditions on the OHC Strength Values

Specimen	B-stage condition	Consolidation		OHC strength (ksi)	
		Temperature	Pressure (Psi) ^b	RT (dry)	177°C (wet)
1	250°C/0.5 h	371°C/1.0 h	200	57.8 ± 2.8	39.7 ± 3.7
2	250°C/1.0 h	371°C/1.0 h	200	59.9 ± 3.0	44.2 ± 1.2
3	300°C/0.5 h	371°C/1.0 h	200	55.0 ± 0.7	44.3 ± 3.3
4	300°C/1.0 h	371°C/1.0 h	200	54.5 ± 2.0	42.1 ± 0.2
5 ^a	RT to 371°C	371°C/1.0 h	200	55.4 ± 2.3	39.6 ± 1.8

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

^b 1 psi = 6.897 KPa.

sulted in a severe loss of processability. In fact, η^* did not decrease during a temperature ramp from 371 to 390°C [see Fig. 2(b)], and this suggested that the crosslinking reactions were completed in the 370°C/0.5-h hold period.

From these results, we can conclude that the residual processability of the PETI-5 matrix resin is indifferent when it is subjected to a broad B-stage window (from 250°C/1 h to 300°C/1 h). The B-stage resin matrix softened at 320°C and exhibited a minimum viscosity at 371°C. At 5–10 min into the 371°C hold, the resin gelled, and the viscosity increased abruptly with fast diminishing processability because of crosslinking reactions. CP had to be applied shortly after the B-stage period to exploit the maximum residual fluidity between 320 and 371°C to achieve complete resin impregnation within the laminate.

The measured OHC strengths are listed in Table III for laminates consolidated under the various B-stage conditions discussed previously. A final 371°C/1-h cure with 200 psi was used in all cases. When the standard deviations were considered, both the RT and 177°C OHC strength values were indistinguishable among the specimens. The 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 previously. They also suggest that the 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 results for specimen 5 in Table III.

Composite OHC strength

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

1. The temperature was ramped from RT to 250°C and held there for 1 h (i.e., the B-stage). In this period, a full vacuum was drawn, but no pressure was applied to the prepreg plies.
2. The temperature was ramped from 250°C to the curing temperature (CT) and held there for 1 h.

In this period, the full vacuum was continued, and a CP was applied at the beginning of the ramp.

3. The specimens were cooled. The vacuum and pressure were relieved when the temperature reached 150°C.

The OHC strengths of the composites fabricated from the two different prepreg sources are compared in Table IV. Each OHC strength reported in the table represents a mean value averaged from three specimens. The standard deviations were similar to those reported in Table III. The laminates fabricated from the Cytec Fiberite prepreps yielded higher OHC strengths at lower CPs. For example, the composites made from Cytec Fiberite prepreps at 370°C with 100 psi exhibited a strength level that was unmatched by those laminates made from NASA LARC prepreps with higher CPs. This was attributed to the differences in the prepreg quality. Among the OHC strengths of the NASA LARC composites at the maximum allowable CT (i.e., 370°C), the RT (dry) and 177°C (wet) values were similar, regardless of the employed CP

TABLE IV
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)
	200	59	44	—	—
370	175	55	44	—	—
	160	56	48	—	—
	100	—	—	62	44
360	185	55	43	—	—
355	—	53	37	—	—
350	200	—	—	58	37
340	—	—	—	45	32
355	175	54	33	—	—
350	—	—	—	57	34
350	150	52	35	—	—

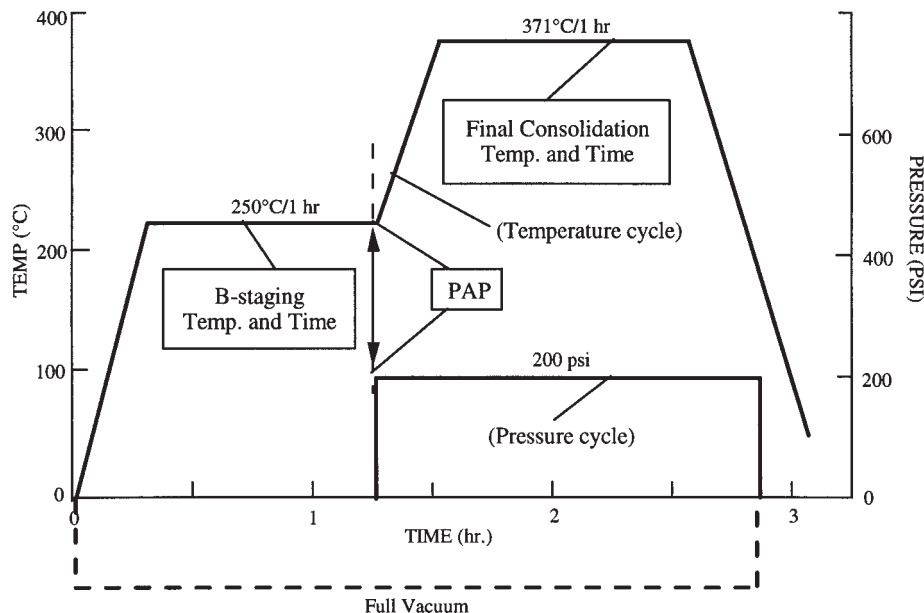


Figure 3 Cure cycle consisting of two-step temperature, one-step pressure, and vacuum profiles.

levels. On the other hand, at the maximum allowable CP (200 psi), 5 and 15% drops for the RT (dry) and 177°C (wet) OHC strengths, respectively, 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.

Determination of the critical curing parameters

A cure cycle consisting of a two-step temperature profile is shown in Figure 3. Curing variables such as

the heating rate, the B-stage temperature and duration, the consolidation temperature and duration, the pressure level and pressure application point (PAP), and their functionalities during composite fabrication are summarized in Table V.

For the IM7/LARC PETI-5 composite fabrication, the molding conditions were restricted to 200 psi and 371°C (700°F) because of the restricted pressure and temperature associated with large commercial autoclaves. Molding variable 1 (i.e., the heating rate in Table V) was essentially fixed at 1–4°C/min for the same reason. On the basis of the aforementioned rheological studies, it was reasonable to keep the prepreg

TABLE V
Critical Molding Variables and Functionalities for Composite Fabrication

Molding variable	Functionalities
1 Heating rate	<ul style="list-style-type: none"> A higher heating rate led to a shorter molding cycle and a more economical fabrication process. However, the processing window could be narrowed for a reactive resin matrix. This was particularly true during the second ramp to 371°C.
2 B-stage temperature	<ul style="list-style-type: none"> A necessary step for volatile depletion before consolidation began. The selected temperature had to be high enough for imidization but low enough to avoid premature advancement of the endgroups' crosslinking reaction.
3 B-stage duration	<ul style="list-style-type: none"> The selected duration time had to be long enough to adequately deplete volatiles.
4 Consolidation temperature	<ul style="list-style-type: none"> The selected temperature must have fully exploited the residual fluidity afforded by the B-stage reactive resin matrix, while conforming to the capacity of the molding equipment. For the PETI-5 matrix, this temperature had to be higher than the meltino temperature ($\approx 350^\circ\text{C}$) of crystallinity generated during the 250°C/1-hr B-stage period.⁷
5 Duration of consolidation	<ul style="list-style-type: none"> The selected duration time had to be long enough to achieve full consolidation of the laminate
6 Consolidation pressure	<ul style="list-style-type: none"> The selected pressure had to be adequate for resin impregnation within the consolidating laminate without causing excessive resin loss.
7 PAP	<ul style="list-style-type: none"> To fabricate a void-free, well-consolidated laminate, the PAP had to be selected for 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 was challenging with reactive resin systems.⁷

TABLE VI
BWCC Design

Run	CT _{coded}	CP _{coded}	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

B-stage conditions (variables 2 and 3 in Table V, i.e., the temperature and duration) unchanged at 250°C and 1 h for this prepreg system.

Furthermore, on the basis of an earlier study that showed that residual volatiles in the prepreps were less than 0.2% (w/w) at the end of a 250°C/1-h B-stage,⁷ PAP (variable 7 in Table V) could safely be selected to be the end of the B-stage period. The pressure was held thereafter to achieve complete resin impregnation within the laminate, and this fully exploited the residual matrix fluidity. A consolidation period (variable 5 in Table V) of 371°C for 1 h was required to afford the complete curing of the PETI-5 chemistry. Therefore, only two variables remained, CT and CP, which were to be optimized in the molding cycle design for the IM7/PETAA-5/NMP prepreg system.

Experimental design

Fractional factorial design was used here to explore the optimal molding window for the IM7/PETAA-5/NMP composite. 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 the laminate consolidation quality. This problem was tackled from the standpoint of response surface methodology.^{10,11} Ultrasonic C-scan images were used to estimate the laminate consolidation quality. A regression analysis was used to estimate the laminate quality at given CT and CP values and to identify optimal combinations of CT and CP in the molding cycle that would likely produce the maximum quality of consolidation.

The 13 experiments shown in Table VI with coded molding variables are organized according to the Box–Wilson central composite (BWCC) design. The selected regions of interest for the two processing variables were 325°C < CT < 371°C and 100 psi < CP < 200 psi. The scaling factors were CT_{scaling factor}

= 16.26°C and CP_{scaling factor} = 35.36 psi. The values of CT and CP for each experiment obtained by the following formulas are included in Table VI:

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

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

A unidirectional 3" × 3" [0]₂₄ composite panel was fabricated under 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 VI. The area percentage so derived is called the C-scan quality (CSQ) for a given panel. The 90% threshold cutoff was chosen on the basis of the experimentally established correlation between the C-scan image and the unidirectional composite consolidation quality. C-scans were measured with identical predetermined conditions for all panels.

Regression analysis

The results in Table V were used to construct the following nonlinear regression equation:

$$CSQ = b_0 + b_1CT + b_2CP + b_{11}(CT)^2 + b_{22}(CP)^2 + b_{12}(CT)(CP) \quad (1)$$

The analysis procedure and the values of the coefficients of eq. (1) are listed in Table VII.

The significance of each term in the regression equation was examined by the standard error and the *t* test. An estimate of the variance (9.62) was also obtained. These values are included in Table VII. A significance with at least a 95% confidence level for each regression coefficient was obtained. The final regression equation can be presented as follows:

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

Optimal molding conditions

CSQ contour surface mapping, based on CT and CP molding variables and generated from eq. (2), is shown in Figure 4. The CSQ value is labeled for each contour curve. Higher CT and CP processing conditions yielded laminates with higher percentage values of CSQ. A processing window can be defined as being bordered by a set of CT, CP, and CSQ contour curves. The processing window yielding 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

TABLE VII
Regression Analysis for the BWCC Design

Experiment	C-scan quality (%)	CT	CP	(CT) ²	(CP) ²	CP × CT
1	0.05	-0.05	-0.05	0.05	0.05	0.05
2	5.05	5.05	-0.05	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	0.07	-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
Standard error	3.41	3.41	3.41	3.65	3.65	4.81
<i>t</i> test	16.18	6.75	8.75	2.33	2.37	2.90
Confidence (%)	99+	99+	99+	95+	95+	97.5+

CSQ percentage decreases with lower CT and CP conditions. This is consistent with the experimental observations. It was reported that double crystalline melting peaks at 290 and 353°C were induced in the PETI-5 resin matrix when it was subjected to 250°C/1-h annealing.⁷ When CT is lower than these crystalline melting temperatures, the residual fluidity is reduced, and the composite processability is likely to suffer in such a situation.

Also included in Figure 4 are discrete RT (dry) and 177°C (wet) OHC strength values measured under several molding conditions, as listed in Table IV. The composite strength values are from the NASA LARC prepreg only for the reasons discussed earlier. These measured strength values exhibited a trend similar to 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. As for the 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 for the laminates fabricated at CT ≥ 350°C. CT is, therefore, a more sensitive molding parameter than CP for the fabrication of the IM7/PETI-5 composite. The regression model correctly predicted such a trend, particularly in the regions in which CT was below 350°C. As CT increased, such sensitivity diminished, as observed from the experimental OHC strength values (i.e., in the regions in which CSQ was greater than 80% and CT was greater 360°C) included in the figure.

CONCLUSIONS

The processing robustness of IM7/PETI-5 was investigated with respect to the prepreg shelf life, the effect of the B-stage conditions, and the optimal processing window. The rheological measurements were useful for the processability evaluation of the ambient-stored prepreps. The prepreg rheology was not affected by prolonged ambient storage (i.e., up to 60 days). Critical prepreg characteristics such as the initial softening temperature of the matrix resin (i.e., ~ 260°C), the minimum viscosity, and the temperature of the minimum viscosity (i.e., 371°C) were all retained by the aged prepreps. Both the RT and 177°C (wet) OHC strength values of laminates were unaffected as well.

The rheological measurements suggest that the processability of the PETI-5 matrix resin is only slightly affected over a wide range of B-stage temperatures (from 250 to 300°C). Both the RT and 177°C (wet) OHC strength values were statistically indistinguishable for the composite specimens B-staged at 250°C for 0.5 h, at 250°C for 1 h, at 300°C for 0.5 h, or at 300°C for 1 h and consolidated at 371°C for 1 h. Such a wide B-stage window allows the IM7/PETI-5 prepreg to accommodate the processing variations associated with the different sizes of the fabrication equipment and composite parts.

The BWCC design was used to optimize the molding conditions for the IM7/PETI-5 composites. The regression model suggests that CSQ increases with higher CT and CP conditions, and this is consistent with the experimental observations. The processing

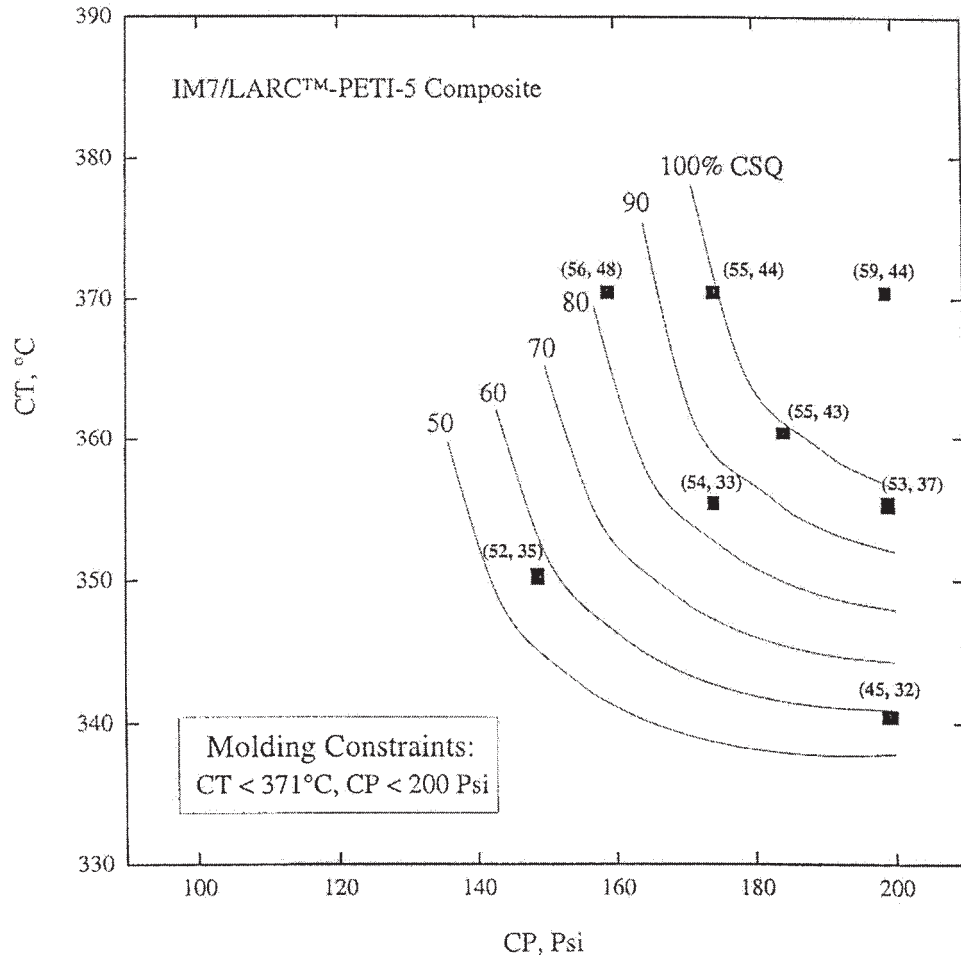


Figure 4 Response surface mapping constructed by the regression model. The first and second values in parentheses represent the RT (dry) and 177°C (wet) OHC strengths, respectively, under each discrete molding condition.

window yielding laminates with 100% CSQ was predicted to be the region bounded by $CP = 200$ psi, $CT = 370^\circ\text{C}$, and the 100% CSQ contour curve. The response surface methodology was found to be a useful tool in process optimization. The IM7/PETI-5 composite was more sensitive to the consolidation temperature than to the CP. At the maximum allowable temperature (i.e., 371°C), good laminate quality was achievable at 100 psi. However, the processability dropped dramatically at consolidation temperatures below 350°C . At 340°C and 200 psi, for example, the RT OHC strength was reduced from a nominal 56 to 45 ksi. This was attributed to the reduced fluidity associated with the semicrystalline matrix, which was generated during the $250^\circ\text{C}/1\text{-h}$ B-stage used throughout this investigation.

The processability of the IM7/LARC 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. When it was subjected to the constraints of a commercial autoclave, the optimal molding conditions were found to be bounded by CT

$\leq 370^\circ\text{C}$, $CP \leq 200$ psi, and a 85% CSQ response surface contour curve derived from a regression analysis.

References

- Hergenrother, P. M. SAMPE J 2000, 36, 30.
- Bryant, R. G.; Jensen, B. J.; Hergenrother, P. M. Polym Prepr 1993, 34(1), 566.
- Jensen, B. J.; Bryant, R. G.; Wilkinson, S. P. Polym Prepr 1994, 35(1), 539.
- Havens, S. J.; Bryant, R. G.; Jensen, B. J.; Hergenrother, P. M. Polym Prepr 1994, 35(1), 553.
- Smith, J. G., Jr.; Hergenrother, P. M. Polym Prepr 1994, 35(1), 353.
- Hergenrother, P. M.; Bryant, R. G.; Jensen, B. J.; Smith, J. G., Jr.; Wilkinson, S. P. Soc Adv Mater Proc Eng Ser 1994, 39, 961.
- Hou, T. H.; Jensen, B. J.; Hergenrother, P. M. J Compos Mater 1995, 30, 109.
- Rommel, M. L.; Konopka, L.; Hergenrother, P. M. Int SAMPE Tech Conf Ser 1996, 28, 1.
- Rommel, M. Northrop Grumman Corp. (Los Angeles, CA). Private communication, 1994.
- Diamond, W. J. Practical Experiment Designs; Van Nostrand Reinhold: New York, 1989; p 237.
- Box, G. E. P.; Hunter, W. G.; Hunter, J. S. Statistics for Experimenters—An Introduction to Design, Data Analysis and Model Building; Wiley: New York, 1978; p 51.