Processing and Properties of A Phenolic Composite System*

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Abstract

Phenolic resin systems generate water as a reaction by-product via condensation reactions during curing at elevated temperatures. In the fabrication of fiber reinforced phenolic resin matrix composites, volatile management is crucial in producing void-free quality laminates. A commercial vacuum-bag moldable phenolic prepreg system was selected for this study. The traditional single-vacuum-bag (SVB) process was unable to manage the volatiles effectively, resulting in inferior voidy laminates. However, a double-vacuum-bag (DVB) process was shown to afford superior volatile management and consistently yielded void-free quality parts. The DVB process cure cycle (temperature /pressure profiles) for the selected composite system was designed, with the vacuum pressure application point carefully selected, to avoid excessive resin squeeze-outs and achieve the net shape and target resin content in the final consolidated laminate parts. Laminate consolidation quality was characterized by optical photomicrography for the cross sections and measurements of mechanical properties. A 40% increase in short beam shear strength, 30% greater flexural strength, 10% higher tensile and 18% higher compression strengths were obtained in composite laminates fabricated by the DVB process.

KEY WORDS: phenolic composite, vacuum-bag process, double-vacuum-bag process, composite cure cycle, composite mechanical properties.

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1. Introduction

Traditional composite fabrication by autoclave is costly in terms of capital investment, and limits the size of the parts that can be produced. One of the attractive out-of-autoclave processes is the oven vacuum-bag process. The vacuum-bag process utilizes atmospheric pressure created by the vacuum suction for laminate consolidation at elevated temperatures. Single-vacuum-bag (SVB) processing is commonly used for molding epoxy matrix based composites because of the absence of reaction by-products or other volatiles. However, the superior fluidity (low viscosity) of epoxy matrix may yield excessive resin flash, which results in dry fibers and extensive void networks in the laminate. Furthermore, SVB processing is often ineffective in composite molding when a reactive resin matrix with volatile by-products or solvent containing prepreg is present. The SVB assembly inherently hinders and/or retards the volatiles depletion mechanisms during fabrication because a compaction force (i.e., atmospheric pressure) is created and exerted onto the laminate during the volatile depleting B-stage period [1-6].

Using a SVB process for composite manufacturing with a reactive resin matrix or a solvent containing prepreg usually consists of a two-step ramp-and-hold temperature profile. These temperature and hold duration steps are unique for a given composite system. The low temperature ramp-and-hold step is called the B-stage. During the B-stage, prepregs are heated and reaction by-products from the resin's chemical reactions are generated. Volatiles (i.e., solvent and reaction by-products) are free to escape because of the absence of applied pressure in this period. The resultant residual volatile content and viscosity of the matrix resin remaining inside the composite are determined by the B-stage conditions. After the B-stage period, a second temperature ramp-and-hold is followed. Pressure is applied during this high temperature ramp-and-hold period to afford laminate consolidation with the desired physical and mechanical properties. Once the consolidation pressure is applied, residual volatiles, if any, are locked in and unable to escape. In order to produce a void-free high quality laminate, the residual volatile content and processability of the resin matrix must be carefully controlled by a workable cure cycle designed specifically for a given composite system.

A double-vacuum-bag (DVB) procedure was first devised at the Naval Air Warfare Center, Warminster, PA about two decades ago to replace the SVB process for aircraft composite repair applications. When bonding the wet lay-up repair patch of epoxy matrix, the double vacuum procedure eliminated problems of excessive flash during the B-stage period [1-4]. Recently, the DVB

process was evaluated for the fabrication of high performance composites with volatile generating reactive resin matrices such as polyimides and phenolics [5-6].

2. Double-Vacuum-Bag Process

A schematic drawing illustrating the concept of the DVB molding assembly for volatile management and composite manufacturing is shown in Figure 1. Fiber reinforced reactive resin matrix prepregs are laid up between the caul and the tool steel plates. They are then enclosed by a vacuum bag (designated as Inner Bag), that is sealed around the edges onto the tool plate. A vacuum port is built on the tool plate inside the Inner Bag and connected to a vacuum pump as with the SVB process. Next a perforated tool is installed outside the perimeter of the Inner Bag. This tool has to be stiff enough to withstand the 101.4 kPa (14.7 Psi) atmospheric pressure created by the vacuum. A second vacuum bag (designated as Outer Bag) is then assembled in the same fashion, with a vacuum port built on the tool plate, which is located between the Inner and Outer Bags and connected to a separate vacuum pump. For the high temperature (371°C curing) resin systems, a Kapton® film of 50 µm (0.002") to 75µm (0.003") in thickness is used as bagging material. This DVB assembly is then placed in a heating chamber and subjected to the proper cure cycle for composite manufacturing.

During the B-stage (i.e., the low temperature ramp-and-hold period), full vacuum (762 mm Hg) is applied to the Outer Bag, while a slightly lower vacuum level (i.e., 711 mm Hg) is set in the Inner Bag. The Outer Bag is collapsed onto the stiff perforated tool due to the atmospheric pressure outside the bags. Because of the vacuum differential between the two bags, the Inner Bag "balloons" and presses against the perforated stiff tool leaving no compaction force, while affording a 711 mm Hg vacuum, on the composite. In the DVB arrangement, the composite lay-up assembly is not compacted by the atmospheric pressure via the Inner Bag, and remains loose. Volatiles are free to escape with the aid of 711 mm Hg vacuum suction from the Inner Bag vacuum pump during the B-stage.

At the end of the B-stage, the Outer Bag is purged to atmosphere, while the Inner Bag vacuum is increased to 762 mm Hg. The Outer Bag is released from the tool, and the Inner Bag collapses onto the caul plate under one atmospheric pressure. This pressure helps to consolidate the laminate during the high temperature ramp-and-hold period of the cure cycle.

The concept of DVB assembly and processing described above can be easily implemented in any vacuum heating chamber such as a vacuum oven, vacuum press or

autoclave [6]. The DVB process was implemented in a vacuum press as shown in Figure 2 in the present study. In this case, one only needs to assemble the Inner Bag for the composite. The chamber wall serves as the Outer Bag, and the stiff perforated tool between the Bags is replaced by the upper platen.
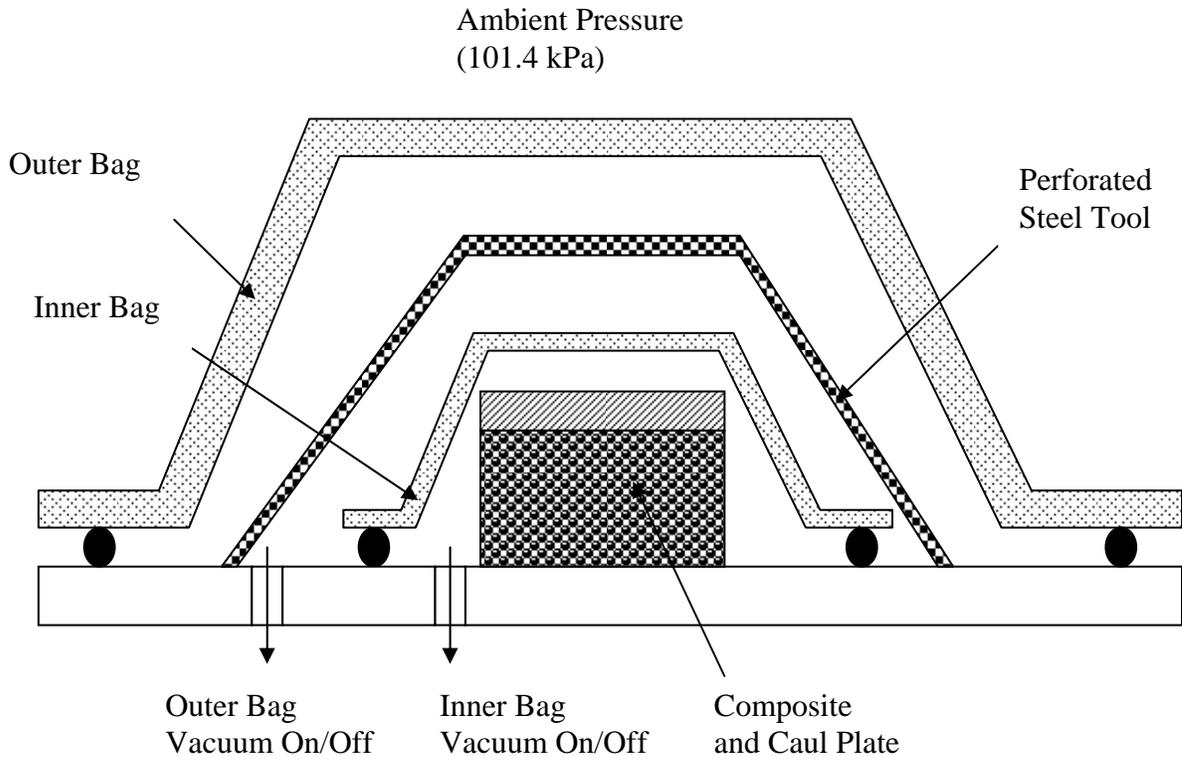

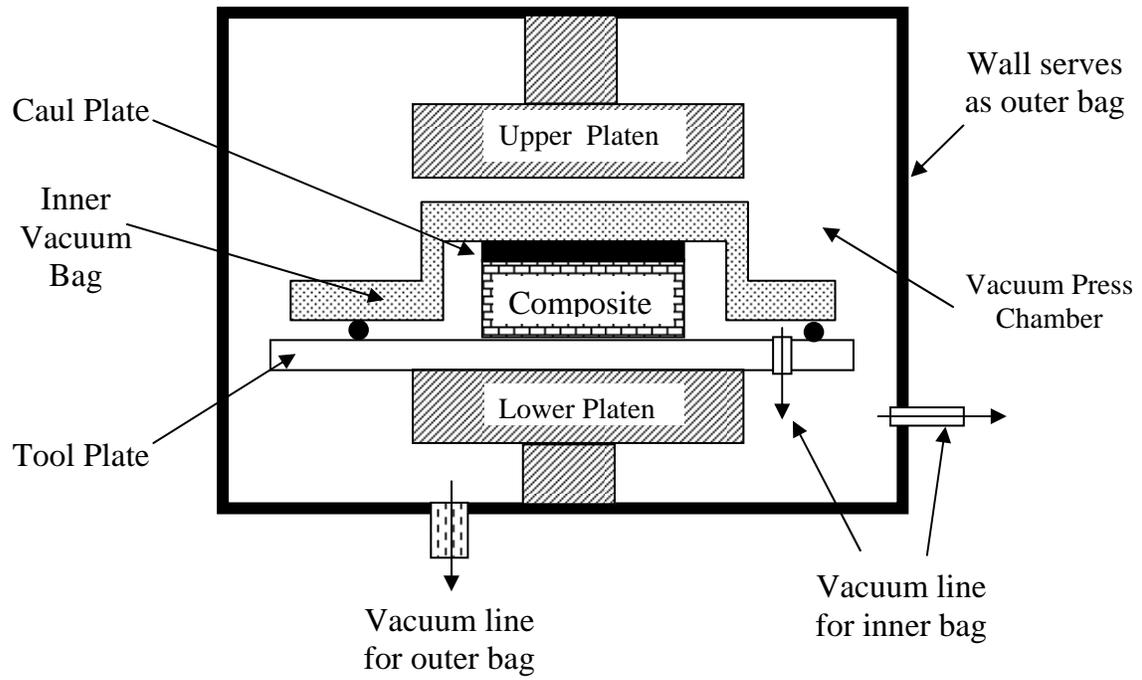Figure 1.   Schematic of DVB assembly.

Figure 2.   DVB process implemented in vacuum press

3. Material

Commercial vacuum-bag processable 7781 E-glass/Cycom® 6070 prepreg (8 harness satin fabric), was received from Cytec Engineering Materials (Anaheim, CA). This prepreg contains 3-5% volatiles. Cycom® 6070 is a 138°C to 160°C (280°F to 320°F) curing phenolic resin. It has a service temperature up to 260°C (500°F) when stepwise post-cured up to 232°C (450°F). Cycom® 6070 is a novolac and releases water as a reaction by-product when curing. Volatiles (water and solvent) management is critical to obtaining high quality, void-free laminates during composite fabrication.

4. SVB and DVB Cure Cycle Designs

The vacuum-bag cure cycle suggested by the material supplier is 15-45 minutes at 559 mm Hg (22" Hg) and 138°C (280°F). A similar SVB cure cycle was used in this study for comparison purposes as shown in Figure 3. Atmospheric pressure created by the vacuum was applied throughout the cure cycle in the SVB molding process.
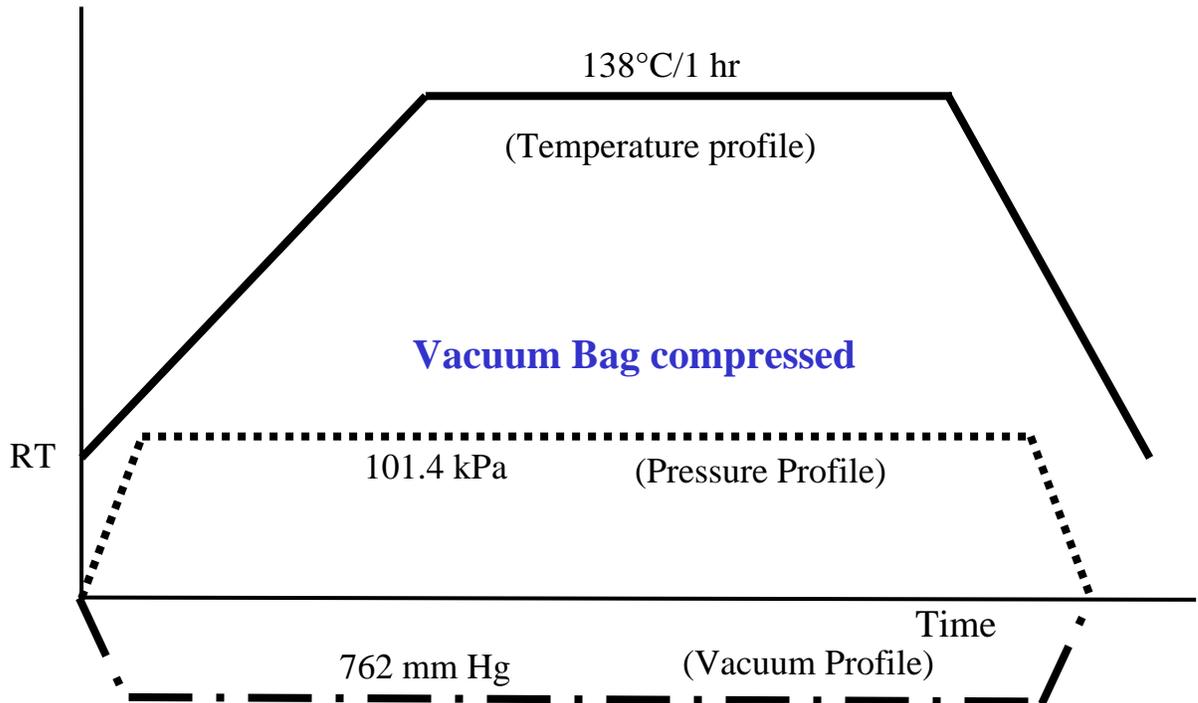

Figure 3.   SVB process cure cycle for molding 7781 E-glass/Cycom® 6070 composite.

The DVB process cure cycle for fabricating this phenolic composite system is shown in Figure 4. A single temperature ramp-and-hold profile was used. The heating rate was 2-4°C/min (5-8°F/min) from RT to 138°C (280°F), followed by 1 hr dwell at temperature and then cool down. The pressure (vacuum) profiles are more complex. During the ramp from RT to 100°C (220°F), the Inner Bag vacuum was 635 mm Hg (25" Hg), while the Outer Bag (i.e., the vacuum press) vacuum was 762 mm Hg (30" Hg). As a result, the Inner Bag

ballooned and pressed against the upper platen of the press. There were no compressive forces against the B-staged prepreg plies, yet the volatiles within the plies were depleted continuously by the 635 mm Hg (25" Hg) vacuum suction during this period.
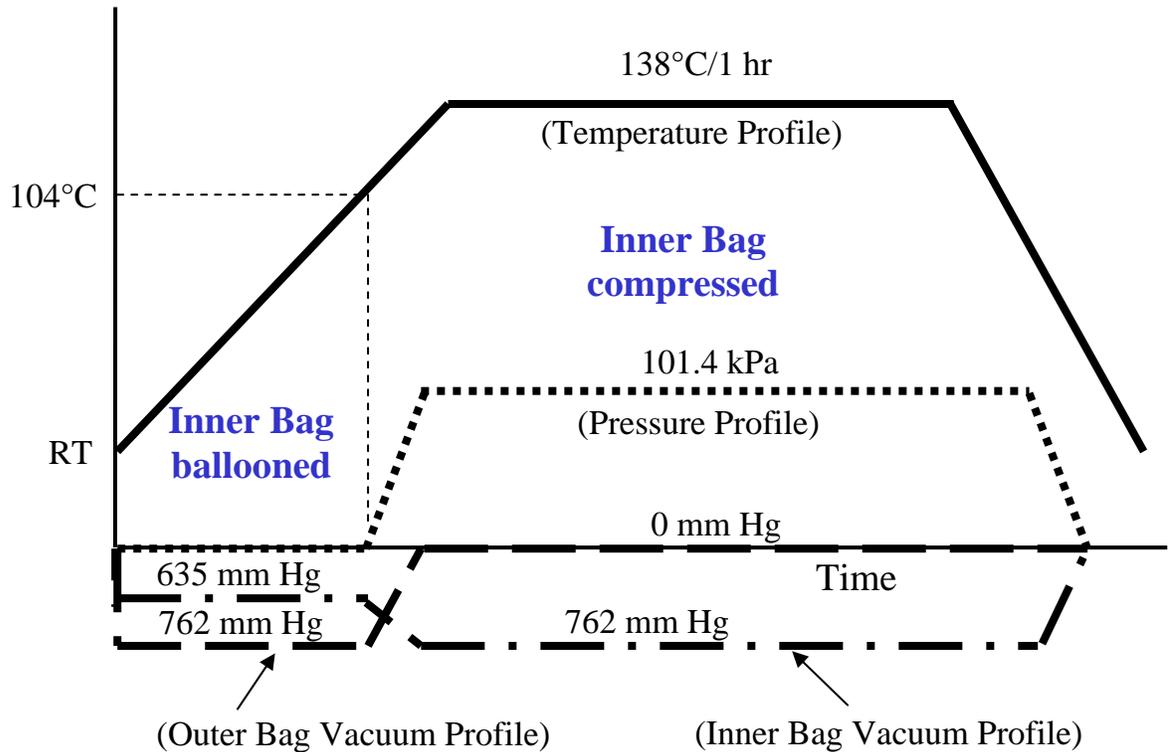

Figure 4.   DVB process cure cycle for molding 7781 E-glass/Cycom® 6070 composite

At 100°C (220°F), the Inner Bag vacuum was increased to 762 mm Hg (30" Hg) while the Outer Bag (i.e., vacuum press) was purged to ambient pressure. The Inner Bag compressed the pre-dried prepreg plies with 101.3 kPa (14.7 Psi) consolidation pressure. This pressure was maintained until the end of the cure cycle. If volatiles were not adequately depleted before the forced consolidation (i.e., during the B-stage period), voids would develop in the consolidation period yielding an inferior laminate. On the other hand, prepreg plies would become un-processable under the vacuum pressure alone if severe B-stage conditions (temperature and time) were employed, leading to a high resin viscosity (i.e., a poor residual fluidity). The application of full vacuum at 100°C (220°F) was determined

from experiments, and was a result of a balance between the degree of volatile depletion and the residual fluidity remaining in the resin matrix after the B-stage [7-13].

5. Results and Discussion

Composite mechanical properties including short beam shear strength (SBS) (ASTM-D2344), flexural strength and modulus (ASTM-D790), tensile strength and modulus (ASTM-D3039) and compressive strengths and moduli (ASTM-D3410) were evaluated at RT and 82°C (180°F). The test matrix is tabulated in Table 1. For comparison purposes, an identical temperature profile as described above was used for the laminate fabrication in both SVB and DVB molding processes. Only the vacuum (i.e., pressure) profiles were different.
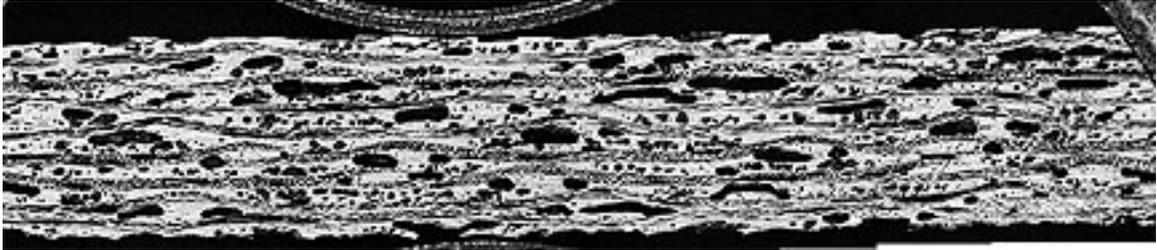
Table 1. 7781 E-glass/Cycom$^®$ 6070 phenolic composite mechanical test matrix.

Mechanical test	Specimen				
	lay-up	Length (cm)	Width (cm)	Temp. (°C)	No. tested at each temp.
SBS	$[0]_{16}$	1.905	0.635	RT, 82	4-7
0° flex*	$[0]_8$	6.985	1.27	RT, 82	4-8
0° tensile	$[0]_8$	25.4	1.27	RT, 82	4-5
0° compression	$[0]_{16}$	15.24	0.635	RT, 82	4

* 0° in warp direction

The cross section photomicrographs of the resultant laminates are shown in Figure 5. High void contents were observed for the SVB molded laminate (Figure 5(a)). The resin-rich domains between fiber tows were particularly high in void content compared to the domains within the tows. Apparently, the SVB process entrapped volatiles in the final consolidated laminate parts. The photomicrograph of the resultant laminate fabricated by the DVB process in Figure 5(b) shows a greatly improved quality part. The DVB assembly and process described above had overcome the deficiencies of the traditional SVB process by affording superb and effective volatile management during the composite B-stage period.

(a) SVB molded laminate (20X)
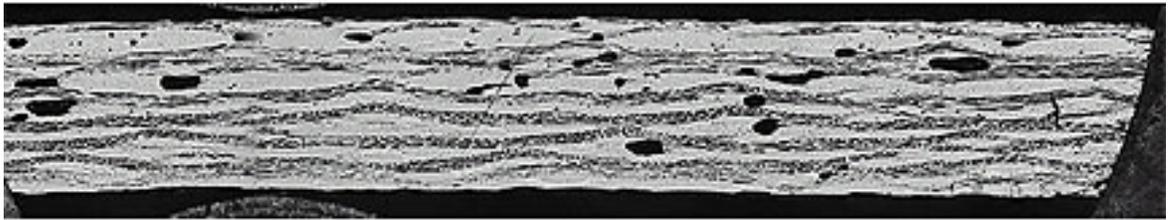

(b) DVB molded laminate (20X)

Figure 5. Optical photomicrographs of SVB and DVB molded
7781 E-glass/Cycom$^®$ 6070 phenolic composites.

Table 2. 7781 E-glass/Cycom$^®$ 6070 phenolic composite mechanical properties.

Mechanical property	Test temp. (°C)	7781 E-glass/ Cycom$^®$ 6070 (from supplier[*])	7781 E-glass/ Cycom$^®$ 6070 (fabricated by **SVB**)	7781 E-glass/ Cycom$^®$ 6070 (fabricated by **DVB**)
SBS strength (MPa)	RT	14.5-15.2	31.0 ± 0.7	44.8 ± 1.4
	82	11.0-12.4	28.3 ± 0.7	42.1 ± 1.4
Flex strength (MPa)	RT	462-510	450.0 ± 20.7	609.0 ± 9.7
	82	421-469	396.6 ± 17.2	520.0 ± 13.8
Flex modulus (GPa)	RT	17.2-26.2	35.2 ± 1.4	33.8 ± 0.7
	82	24.1-26.9	31.0 ± 6.9	31.0 ± 1.4
Tensile strength (MPa)	RT	407-421	362.8 ± 15.2	393.8 ± 15.2
	82	345-359	346.9 ± 11.0	383.5 ± 23.5
Compression strength, (MPa)	RT	317-359	320.0 ± 11.7	378.0 ± 20.0
	82	255-290	284.2 ± 19.3	336.6 ± 4.1

* Cycom$^®$ 6070 Phenolic Resin Technical Datasheet, January 29, 2002, Cytec Engineered Materials, Anaheim, CA

Mechanical properties are tabulated in Table 2. Also included in the table are properties provided by the material supplier. Except for SBS strength, flex modulus and RT tensile strength, the properties at both RT and 82°C (180°F) for laminates fabricated by the SVB process are comparable to those from the supplier. Composites fabricated by the SVB process exhibited properties either equal or higher than the material supplier's values at both temperatures, except for the RT tensile strength where a 10% reduction in measurement was obtained.

The DVB process yields all measured mechanical properties consistently higher than the SVB process. The following improvements were observed: 45% higher in SBS strength, 35% higher in flex strength, and 8.5% higher in tensile strength at RT. At 82°C, 49% increase in SBS strength, 31% increase in flex strength, and 10.5% increase in tensile strength were measured. Compression strength were 18% greater at both temperatures. It was noted that the tensile strength values showed the smallest percentage increases among these measurements. This was probably due to the fact that tensile strength is a fiber dominant property.

6. Conclusions

DVB processing technology is a simple and cost effective extension of the traditional SVB process in composite fabrication. Although the DVB process is similar to the SVB process in that it uses vacuum alone for composite consolidation, the DVB process has the advantage of eliminating the excessive resin squeeze-outs resulting in precision net shape control of the prepreg plies during B-stage. In addition, it affords inherent volatiles depletion mechanism, superior to the SVB process, yielding void-free quality laminate parts not possible by SVB. The DVB technique eliminates size limitations, costly tooling and high capital expenditures required for the conventional autoclave composite fabrication.

The DVB process has been implemented in a vacuum press for a phenolic resin matrix composite fabrication in this study. The choice of using a vacuum press instead of an oven is because of its simple implementation. Comparisons were made between the SVB process and the DVB process by using identical temperature profile design in the cure cycles. Photomicrographs of the laminate cross sections revealed that significantly fewer voids existed in DVB molded specimens. The DVB molded specimens also exhibited enhanced mechanical properties at both RT and 82°C (180° F) compared to the SVB molded counterparts: 40% higher in SBS strength, 30% higher in flexural strength, 10% higher in tensile strength and 18% higher in compression strength values.

This study demonstrated that the DVB process is superior to the traditional SVB process in volatile management during composite fabrication. The DVB process technology is particularly useful in the fabrication of composites with reactive resin matrices such as polyimides and phenolics. These classes of materials generate reaction by-products (i.e., water) during curing. These by-products, together with the carrier solvent, can be effectively managed by the DVB process to yield void-free quality laminates.

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